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DEPARTMENT OF COMMERCE

UNITED STATES BUREAU OF MINES
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INFORMATION CIRCULAR

BARITE AND BARIUM PRODUCTS

PART II. BARIUM PRODUCTS

BY

R. M. SANTMYERS

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BARITE AND BARIUM PRODUCTS[1]

Part II. Barium Products

By R. M. Santmyers[2]

CONTENTS

	Page
Introduction	2
Ground barite	3
Preparation	3
Uses	3
Production	4
Market and prices	5
Imports and exports	7
Lithopone	8
Preparation	8
Use	9
Production and sales	10
Market and prices	11
Imports and exports	12
Correlation of sales of barium pigments with lead and zinc pigments	13
Barium chemicals	15
Preparation	15
Uses	17
Production and sales	18
Market and prices	21
Imports and exports	21

1/ The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is used: "Reprinted from U. S. Bureau of Mines Information Circular 6223."

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INTRODUCTION

Barium is derived from two minerals, barite (barium sulphate) and witherite (barium carbonate). Metallic barium is at present of little commercial importance, although small quantities are used as a scavenger of gases in the manufacture of radio tubes and as a hardening agent for lead; however, barium compounds, many of which are manufactured from the minerals by chemical processes, constitute an important class of commercial products and enter into both domestic and foreign trade in considerable quantities.

Barium products may be roughly divided into three classes: (1) Ground barite; (2) lithopone; and (3) barium chemicals. Ground barite - crude ore which has been washed, jigged, and ground very fine - is used as a filler in numerous substances, such as paper, paints, rubber, etc., where a heavy, chemically inert substance is required. Lithopone - a mixture of approximately 70 per cent barium sulphate, 26 to 28 per cent of zinc sulphide and 1 to 3 per cent of zinc oxide - is a widely used white pigment. Barium chemicals find employment in a wide variety of industries. The manufacture of lithopone, at present, consumes by far the larger part of the crude barite produced and imported into this country and has expanded rapidly in recent years. Prior to the war the entire lithopone industry of the United States was located along the Atlantic coast practically at tidewater. The barite required by the industry was supplied by imports, chiefly from Germany, as the imported material cost less than domestic barite. War conditions forced lithopone manufacturers to develop deposits in Georgia, Tennessee, South Carolina, and elsewhere in the Southern States in order to obtain supplies of raw material. At the same time the manufacture of lithopone was started in the Middle West, utilizing crude barite from Missouri. With the termination of the war and the reappearance of German barite on the American market, the Southern field is finding it more and more difficult to furnish the eastern lithopone industry with crude ore.

The list of commercial barium chemicals includes blanc fixe or artificial sulphate of barium, barium carbonate, chloride, nitrate, monoxide, dioxide, hydroxide, sulphide, chlorate, and chromate. A few of these chemicals, however, are of only small importance. Barium sulphide (an intermediate product from which the majority of the other barium chemicals are made), blanc fixe and barium dioxide, chloride, nitrate, carbonate and hydroxide are the barium chemicals that are used extensively.

Prior to the war the United States was wholly dependent on imports for its supply of barium chemicals. Germany was the largest producer and furnished about two-thirds of the domestic requirements. Between 80 and 90 per cent of the imports were represented by three barium salts - barium carbonate, barium chloride, and barium dioxide. The cessation of imports and the war demand for barium chemicals (barium nitrate, blanc fixe, and barium dioxide) resulted in the establishment of a barium chemical industry in this country.

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Domestic plants were erected chiefly in the East and Southeast, although there were plants in Ohio and Illinois. In some cases the plants were located relatively close to the domestic deposits of barite. The chief markets for barium chemicals were in the East, and upon the termination of the war domestic products came into direct competition with imported chemicals. The eastern plants are so situated that they can use either imported or domestic barite as raw material, and therefore are able to compete with imported barium chemicals.

Those plants located close to the southern barite deposits and those in the Middle West depend solely on domestic crude barite which costs more than that imported from Germany. In these areas the higher cost of raw materials, however, is partly offset by the fact that although barium chemicals are not particularly bulky, differences in freight rates tend to equalize the final costs of the domestic and foreign products.

GROUND BARITE

Preparation

The preparation of ground barite varies in different plants and according to the condition of the ore. The general practice, however, is to crush the ore to about 1 inch and by log washing to remove the clay and earthy material. Often this washing is done at the mine and need not be repeated at the grinding mill. The next step is to grind the cleaned material, usually in tube mills; then the ground barite, suspended in water, is either screened or water floated in order to remove any coarse particles. If off-color, the finely ground barite is bleached with sulphuric acid, which removes the stains due to oxides of iron. After being washed several times with water, the bleached product is dried, pulverized, and packed in bags or barrels. Very little labor is required in the process of grinding after the ore is placed in the first or primary crusher until it reaches the packing room. The barite is conveyed mechanically or pumped, suspended in water, through the different processes.

Uses

The principal use of ground barite is as a filler. Since it is extremely heavy, chemically inert and white, it is admirably fitted for this purpose. The paint, paper, rubber, linoleum, and cloth industries all use considerable quantities to add weight and body to their products. By far the larger part - estimated at 50 to 70 per cent - of all the ground barite produced and sold in the United States is consumed in the paper and rubber industries.

As a rubber filler, bleached or unbleached, ground barite is employed where a soft rubber article is desired, as in rubber bands, tubing and the like, but not where strength and resistance to abrasion is required, as in auto tires. The bleached form is used in papers where weight is desirable with a high finish, as in Bristol board, playing cards, and plate paper. Natural barite is not often used in high-grade paints, but a limited quantity is employed in the cheaper grades and a small amount of the bleached mineral is used directly as an extender and loader and as a base for lake colors.

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Finely ground barite mixed with a colloidal clay, such as bentonite, and a suitable suspending medium is effective in making up heavy liquids used as a seal in drilling for oil and gases. The heavy liquid holds back the gas flow until the casing can be placed. Finely divided iron oxide in suspension is employed for the same purpose.

A limited amount of unbleached ground barite is used in molded goods, such as buttons and hard rubber articles. One of its newer uses in the molded hard-rubber industry is as a component part of the protecting hard-rubber shield around X-ray tubes. Because of its high density, ground barite tends to absorb the rays and thereby protect the operator, except where the shield is open. Plaster containing a large admixture of ground barite is used on walls of X-ray rooms in order to limit the radiation of the rays. It is also used in making brick for the construction of X-ray laboratories, replacing in both cases the lining of sheet lead used to prevent the rays from escaping and doing possible injury.

Barium platino-cyanide has the property of becoming fluorescent under the action of X-rays and ultra-violet light rays. This barium compound is used in X-ray photography by coating the projecting screen with it. The shadows made by the rays are thus outlined on the screen.

A small quantity of ground barite is used in the manufacture of artificial ivory. Some barite is used as a flux in brass smelting, and is also used in the extraction of iron in reclaiming brass from junk.

Production

The production of ground barite has increased during recent years, but not as rapidly as the production of crude barite. During the years 1915 to 1920 from 31 to 50 per cent of the crude ore consumed in all industries was used for the manufacture of ground barite, but during the years 1921 to 1928 the proportion was only 20 to 29 per cent of the total. This decrease in the percentage of crude barite used for grinding is not due to any great extent to an increase in the imports of ground barite, but to a tremendous growth that that has taken place in the lithopone industry since 1922.

Table 1 and figure 1 show the amount of crude barite used in the manufacture of ground barite, and the percentage of the total for the years 1915 to 1928:

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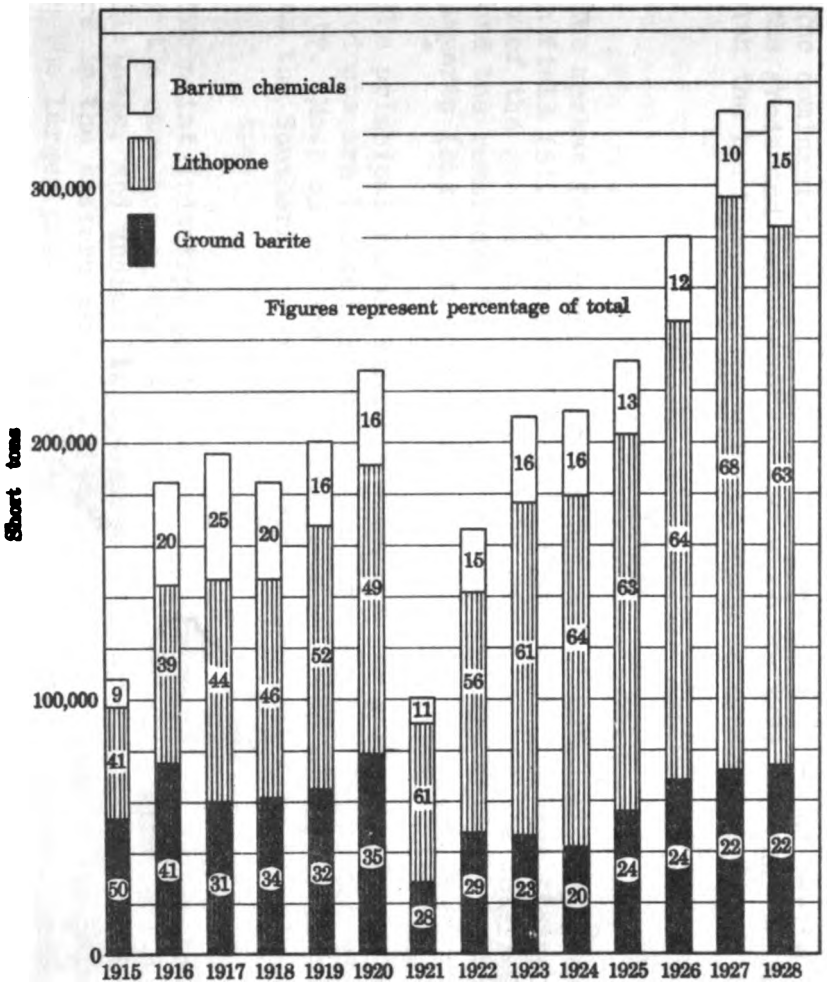

Figure 1. – Crude barite used in the manufacture of barium products

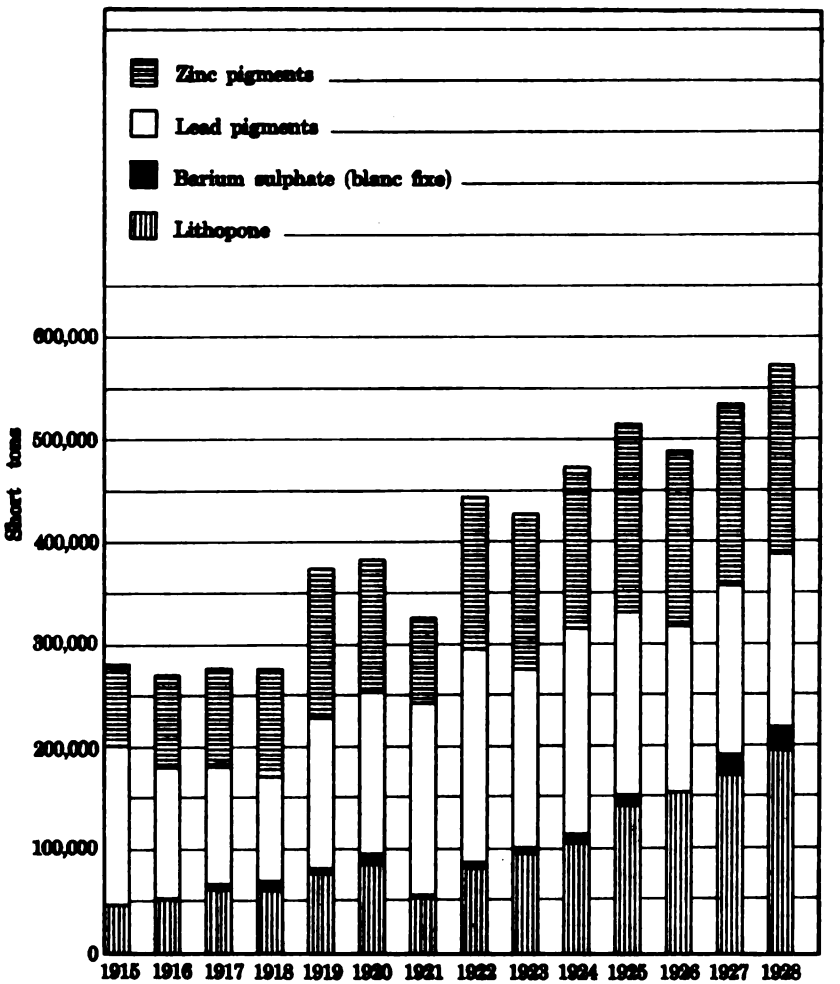

Figure 2. – Sales of barium, lead, and zinc pigments

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Table 1. - Crude barites, both domestic and imported, used in the manufacture of barium products, 1915-1928 (in short tons)

Year	Used for grinding	Total used	Per cent of total
1915	53,903	108,622	50
1916	75,507	185,688	41
1917	60,132	196,039	31
1918	62,440	185,763	34
1919	64,922	201,586	32
1920	79,052	229,443	35
1921	28,296	100,607	28
1922	48,280	167,842	29
1923	47,713	210,587	23
1924	42,855	213,163	20
1925	56,851	232,685	24
1926	69,048	281,056	24
1927	73,119	330,190	22
1928	74,814	334,695	22

The grinding of barite is carried on chiefly in Missouri, which in recent years has produced 30 to 85 per cent of the barite ground in the United States from domestic ore. The other States which produce ground barite are Georgia, 5 to 6 per cent of the total; California, 4 to 6 per cent; and South Carolina, 6 to 8 per cent.

The dominant position held by Missouri in the ground barite industry is due to the grade and texture of the ore which is soft and easy to grind as compared with the hard crystalline variety found in other sections of the country.

Market and Prices

The market for ground barite is divided about equally between the Mid-Western field (St. Louis to Chicago) and the Atlantic Coast States. About 50 per cent of the ground barite used in the eastern market is supplied from Missouri, and the remainder is obtained in part from the Southern field and in part from imports (chiefly from Germany).

The principal rubber manufacturers who use ground barite as a filler in their products are located in and around Akron, Ohio, and in the vicinity of New York City. Most of the ground barite used by these companies is from Missouri, as the Southern ore enters into the rubber industry in only small quantities.

The paint industry, on the other hand, although it is located in practically the same two districts as the rubber industry, also includes Michigan, Illinois, and Indiana in the mid-western market, and Pennsylvania and Delaware in the eastern market. Though Missouri furnishes the paint industry with the larger part of its barite requirements, a greater proportion of Southern ore is used in this industry than in the rubber industry.

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The price of ground barite has remained almost stationary in recent years; the average annual price as reported by producers to the Bureau of Mines ranges between $20 and $22 per short ton. Prior to the war the price ranged from $11.19 per ton in 1908 to $14.18 in 1913, and when hostilities began the price dropped to $12.95 in 1914 and then to $12.32 in 1915, but immediately advanced until in 1918 it reached $18.91 per ton.

Table 2. - Ground barite sold by producers in the United States,[1] 1908-1928

Year	Quantity short tons	Value	Average price
1908 [2]	28,415	$ 318,096	$11.19
1909 [2]	34,673	455,506	13.14
1910 [2]	38,165	475,001	12.45
1911 [2]	39,611	503,867	12.72
1912 [2]	38,225	495,895	12.97
1913 [2]	37,033	525,300	14.18
1914 [2]	35,815	463,858	12.95
1915 [2]	51,557	635,318	12.32
1916	65,440	964,802	14.74
1917	52,694	951,220	18.05
1918	55,086	1,041,608	18.91
1919	[3] 57,985	1,163,437	20.06
1920	65,748	1,381,868	21.02
1921	27,661	622,871	22.52
1922	46.176	933,722	20.22
1923	39,605	895,095	22.60
1924	38,296	784,881	20.50
1925	49.674	1,040,461	20.95
1926	57,812	1,186,563	20.52
1927	57,658	1,166,294	20.23
1928	64,425	1,332,228	20.68

[1] From domestic and imported ore.
[2] Sales of refined barite (domestic only).
[3] Figures cover production, not sales (1919).

Table 3 shows the prices of ground barite per long ton, washed and water floated, f. o. b. plants, bags extra, as quoted from the Engineering and Mining Journal.

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Table 3. - Prices of Ground Barite (Washed and Water floated, f.o.b. mines, bags extra) for Georgia and Missouri, by year, each month.

	Georgia		Missouri					
	1928	1929	1924	1925	1926	1927	1928	1929
Jan.		$19.00	$26 $28	$23 $24	$23	$23	$23	$23
Feb.		$19.00	$23 $24	$23 $24	$23	$23	$23	$23
Mch.	$19.00	$19.00	$23 $25	$23 $24	$23	$23	$23	$23
Apr.	$19.00	$19.00	$23 $25	$23 $24	$23	$23	$23	$23
May	$19.00	$19.00	$23 $24	$23 $24	$23	$23	$23	$23
June	$19.00	$19.00	$23 $24	$23 $24	$23	$23	$23	$23
July	$19.00	$19.00	$23 $24	$23 $24	$23	$23	$23	$23
Aug.	$19.00	$18.00	$23 $24	$23 $24	$23	$23	$23	$23
Sept.	$19.00	$18.00	$23 $24	$23 $25	$23	$23	$23	$23
Oct.	$19.00		$23 $24	$23 $24	$23	$23	$23	
Nov.	$19.00		$23 $24	$23 $24	$23	$23	$23	
Dec.	$19.00		$23 $24	$23 $24	$23	$23	$23	
Average:	$19.00		$23.88	$23.58	$23	$23	$23	
High	$19.00	$19.00	$28.00	$24.00	$23.00	$23.00	$23.00	
Low	$19.00	$19.00	$23.00	$23.00	$23.00	$23.00	$23.00	

IMPORTS AND EXPORTS

The following Table No. 4 shows the imports of ground barite for consumption for the years 1910 to 1928, inclusive.

The imports of ground barite, though formerly important, now play only a small part in the ground barite industry of the United States. Since 1923 they have never exceeded 3,000 tons in any one year. The declared value per ton, as reported in the statistics, plus freight, duty and other charges, indicates that the apparent delivered cost is as high, or higher, than the price obtained for the domestic product.

As previously stated, about 50 per cent of the production of ground barite is consumed along the Atlantic seaboard where it comes in direct competition with German ground barite, but due to the careful preparation of the domestic product as regards fineness, uniformity of quality, etc., and the fact that shipments are made promptly from stocks at American mills, Germany has failed to obtain as strong a foothold in the ground barite industry as it has in the case of crude barite.

There are no recorded exports of ground barite, though it is understood that small quantities are shipped to paint, paper and rubber plants in Canada.

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Table 4. - Imports of ground barite for consumption in the United States, 1910-1928

Year	Rate of duty	Quantity short tons	Value	Price per ton
1910	$5.25 per ton	3,023	$ 27,191	$ 8.99
1911	do	3,655	26,462	7.24
1912	do	3,012	21,642	7.19
1913	do	5,145	36,819	7.16
1914 1/	do	1,107	7,520	6.79
1914 2/	20 per cent ad va-	4,919	35,105	7.14
1915	do lorem	1,966	14,997	7.63
1916	do	-	2	-
1917	do	235	3,813	16.23
1918	do	-	-	-
1919	do	-	-	-
1920	do	245	3,017	12.31
1921	do	895	16,942	18.93
1922 3/	do	3,027	43,392	14.34
1922 4/	$7.50 per ton	1,166	16,061	13.77
1923	do	5,377	88,736	16.50
1924	do	2,527	38,292	15.15
1925	do	2,860	40,008	13.99
1926	do	2,988	44.781	14.99
1927	do	2,910	38,568	13.25
1928	do	2,766	33,378	12.07

1/ From July 1 to Oct. 3, 1913.
2/ From Oct. 4, 1913 to June 30, 1914.
3/ From Jan. 1, 1922, to Sept. 21, 1922.
4/ From Sept. 22 to Dec. 31, 1922.

LITHOPONE

Preparation

The basic raw materials necessary for the manufacture of lithopone are crude barite; coal, coke, or petroleum breeze; zinc; and sulphuric acid. Other chemicals, such as ferric oxide, alumina, lime, and magnesia are required in the process of manufacture, but in minor quantities. Large quantities of clean, soft water are required in making up solutions and in the washing of lithopone to remove soluble impurities. The manufacture of lithopone requires the preliminary production of a solution of barium sulphide and a solution of zinc sulphate. For the preparation of barium sulphide, the crude barite is first crushed and mixed with the proper proportions of pulverized coal or other forms of carbon. This proportion varies slightly with individual manufacturers; it is generally one part of coal to four parts of barite by weight. After heating the mixture for about four hours in a rotating furnace, the barium sulphate is reduced to barium sulphide. The crude sulphide (black ash), which contains about 70 per cent barium sulphide, is then treated with hot water, and the resulting solution of barium sulphide is clarified.

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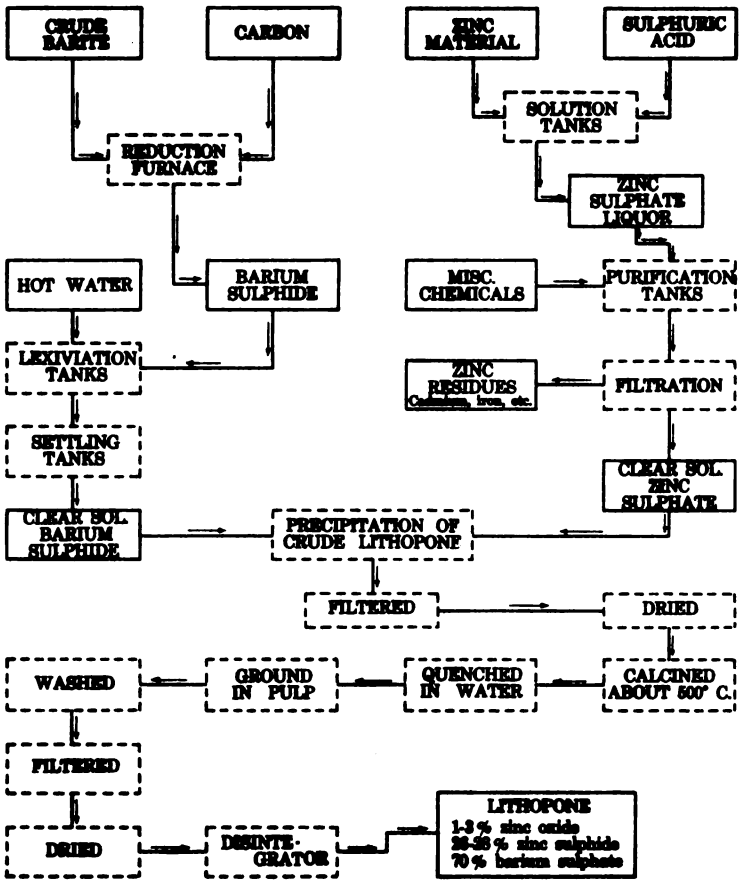
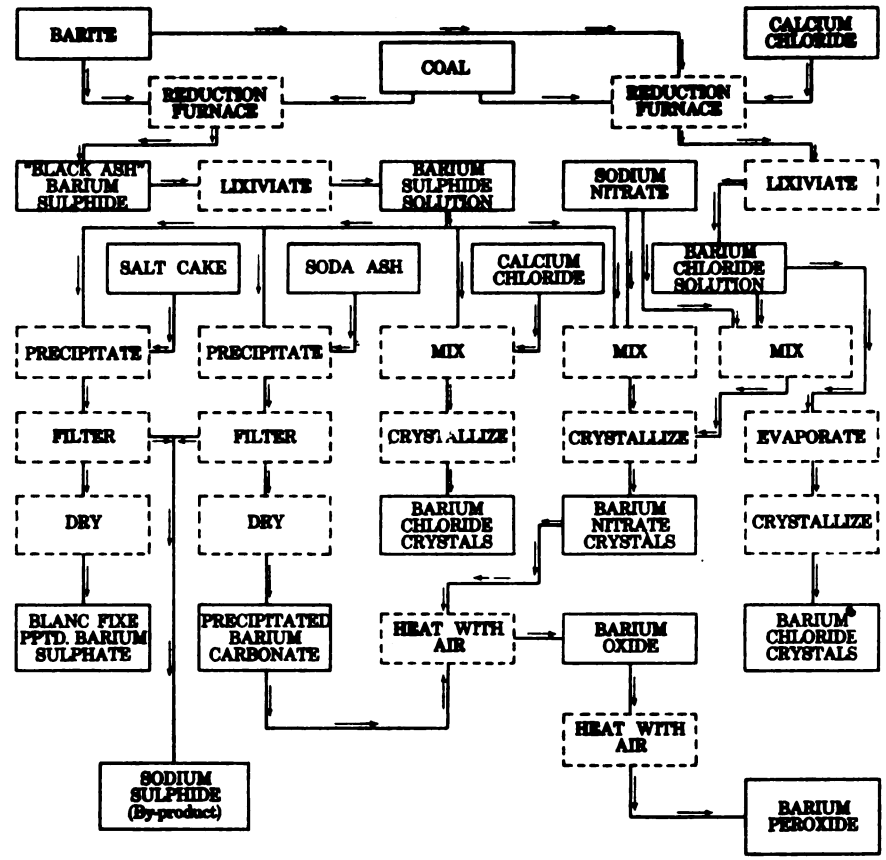


LEGEND

Solid lines.----Raw, intermediate, or finished products
Broken lines.--Apparatus, or steps in process

Figure 3. – Flow sheet for the manufacture of lithopone



LEGEND

Solid lines.----Raw, intermediate, or finished products
Broken lines.--Apparatus, or steps in process

Figure 4. – Flow sheet of the barium chemical industry

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The zinc sulphate solution is prepared by dissolving zinc--in the form of zinc ash, scrap, skimmings, slab zinc, or roasted ore--in dilute sulphuric acid. Since the zinc materials usually contain as impurities other metals (iron, copper or cadmium) which would form colored products on treatment with barium sulphide, the zinc sulphate solution must be purified. Various chemicals are used for this purpose, and this purification, since it represents one of the most important steps in the entire process of manufacture, requires careful chemical control.

Crude lithopone is precipitated from the purified zinc sulphate solution as a white insoluble substance by adding a hot solution of barium sulphide. The crude lithopone is filtered off, dried, and then calcined at about 500° C. in a muffle furnace, which may or may not utilize waste heat from the barite reduction furnace. The hot lithopone is thrown into water, ground, washed several times with water to remove soluble impurities, filtered, and dried. After being run through a disintegrator and reduced to a fine powder, the dry product is packed in bags or barrels for shipment. In some cases the lithopone is air-floated to insure a uniform product. The process is shown graphically in Figure 3.

The value of lithopone depends upon the amount of zinc sulphide in it as well as upon the fineness and whiteness of the product.

Following are several analyses of typical samples of lithopone:

Content	German	English4/	
	1	2	3
$BaSO_4$	64.36	67.59	72.80
ZnS	30.98	27.82	24.14
ZnO	0.55	1.82	0.88
Not reported	4.11	2.77	2.18
	100.00	100.00	100.00

Inferior qualities sometimes contain natural barite which reduces the opacity and covering power and causes them to give a yellowish-white tint when used in linoleum. The natural mineral may be detected by means of the microscope, the precipitated barium sulphate appearing as a fine powder composed of minute crystals of uniform size, whereas the natural barite consists of transparent irregular fragments of larger size.

Uses

Lithopone is used extensively as a white pigment in flat and enamel wall paints for interior use. It is also used in large quantities as a filler in rubber goods, paper, linoleum, oilcloth, and in window-shade cloth. Lithopone has not been used extensively in outside paints because it darkens when

4/ Jour. Soc. Chem. Ind., Sept. 15, 1902, p. 1145
Kochs, E., and Seyfert, F., Pigments and Paints.

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exposed to sunlight or excessive moisture. It usually becomes white again, however, upon drying out, and several brands of lithopone paint have been placed on the market in recent years which are said to withstand exposure to sunlight and moisture.

Production and Sales

The rapid growth during recent years in the output of crude barite was the direct result of a remarkable and rapidly increasing demand for lithopone as a paint pigment.

Table 5 shows the amount of crude barite used in the manufacture of lithopone and the ratio of this consumption to the total barite used in all industries for the years 1915 to 1928, inclusive.

Up to and including the war period the amount of crude barite used for the manufacture of lithopone never exceeded 50,000 short tons annually, while the percentage consumed in this industry never exceeded 46 per cent. Since the war, however, the tonnage of crude barite sold for this use increased rapidly until in 1928, 211,592 short tons were consumed. The percentage of the total consumed in all industries likewise advanced rapidly, until in 1927 68 per cent of the total sales of crude barite were used in the manufacture of lithopone (63 per cent in 1928).

Table 5. - Crude barite, both domestic and imported, used in the manufacture of barium products, 1915-1928 (in short tons)

Year	Used in lithopone	Total used	Per cent of total
1915	44,503	108,622	41
1916	71,898	185,688	39
1917	86,065	196,039	44
1918	85,282	185,763	46
1919	103,688	201,586	52
1920	113,181	229,443	49
1921	61,359	100,607	61
1922	94,259	167,842	56
1923	128,547	210,587	61
1924	137,127	213,163	64
1925	146,693	232,685	63
1926	178,889	281,056	64
1927	222,791	330,190	68
1928	211,592	334,695	63

The marketed production of lithopone has followed closely the sales of crude barite to the lithopone manufacturers, the sales totalling 8,000 to 10,000 tons less annually than that reported as consumed for its manufacture. As may be seen in Table 6, the marketed production prior to the war never exceeded 30,000 short tons, the average for the years 1910 to 1913 being 20,856 short tons. During the war period (1914 to 1918) the production increased rapidly, due to the growing demand and the discontinuance of lithopone imports.

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The average for this five-year period was 51,344 tons, an increase of 146 per cent over the pre-war period. Following the war, the marketed production fluctuated considerably until after the general depression year 1921, when production returned to its normal growth. The average production for this period (1919 to 1928) increased to 119,319 short tons, an increase of 133 per cent over the pre-war period.

The price per ton obtained for lithopone on the American market advanced rapidly with the advent of war until in 1920, the all-time high price of $139.69 per ton was reached. Since then, however, the price has again fallen to a normal increase over that of the pre-war period, the price in 1928 reaching $95.15 per ton.

Table 6. - Marketed production of lithopone, 1910-1928, in short tons

Year	Quantity	Value	Price per ton
1910	12,655	$ 916,512	$ 72.42
1911	13,866	1,243,108	73.70
1912	24,220	1,702,119	70.28
1913	29,685	2,170,445	73.12
1914	32,819	2,490,530	75.89
1915	46,494	3,760,472	80.88
1916	51,291	5,798,927	113.06
1917	63,713	7,406,896	116.25
1918	62,403	7,923,276	126.97
1919	73,365	10,218,850	130.40
1920	89,373	12,484,925	139.69
1921	55,016	6,281,563	121.45
1922	83,360	9,214,040	110.53
1923	98,199	11,608,443	118.21
1924	109,469	12,531,397	114.47
1925	145,019	15,186,147	104.72
1926	159,931	16,062,197	100.43
1927	176,994	17,163,620	96.97
1928	200,468	19,073,914	95.15

Market and Prices

The demand for lithopone, though well distributed throughout the United States, is concentrated chiefly along the Atlantic seaboard, in the Middle-Western States (from St. Louis to Chicago), and in the Pacific Coast States, principally California and Washington.

Prior to the war the lithopone requirements of the United States were furnished almost solely by eastern plants using both domestic and imported crude barite. The imported ore, however, was delivered to consumers at a price much lower than that of the domestic material. Before the war Missouri was the principal source for crude ore for lithopone requirements in the East, which necessitated a long freight haul to the lithopone plants on the Atlantic seaboard.

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With the advent of war, crude barite imports ceased, and the eastern manufacturers of lithopone, in order to secure a source of raw material, developed the barite deposits in the Southern States, principally those in Georgia, Tennessee, and Kentucky.

Later, in order to meet the growing demand for lithopone in the Mid-Western States, eastern paint manufacturers constructed plants at St. Louis, Mo., and in neighboring States, utilizing locally produced crude barite. This new industry expanded rapidly and with the termination of the war was able to hold its own in seeking an outlet for its finished product.

About 1926 the lithopone industry was started in California using locally produced barite, and as the industry did not meet with competition from either the Missouri or eastern products it prospered.

Table 14 shows the prices obtaining for lithopone for the years 1922 to 1928, as quoted by the Oil, Paint and Drug Reporter. A slight decrease is noticeable during this period. In 1922 the price ranged from 6 to 6¼ cents per pound, f. o. b. New York, and represented a slight decline from the prices quoted in the preceding year. In 1923 and again in 1924, there were marked advances, the price ranging from 6 to 7¼ cents per pound during the former year, and from 6-3/8 to 8-5/8 cents during the latter year. In 1925, however, quotations dropped to 6-1/8 to 6-5/8 cents, and in 1928 the prices ranged from 5-3/4 to 5-7/8 cents, the lowest price for this product over a range of 10 years.

Imports and Exports

The imports of lithopone into the United States have never exceeded 11,000 short tons a year.

Table 7 shows the tonnage, the declared value, and the average price per ton for the years 1913 to 1928, inclusive. Prior to 1913, the imports of lithopone were included in the figures for "zinc sulphide white."

With the entrance of the United States into the World War the imports of lithopone ceased entirely, the material having come principally from Germany. In 1919, when business relations were again restored, the United States imported only 739 tons, valued at $122,708, or the high price of $166.05 per ton; but in 1922 the imports had grown to 10,763 tons, valued at $885,671, or $82.29 per ton, representing less than half the price per ton of 1919. In 1923 the imports were 10,440 tons, valued, however, at only $776,383, or $74.37 per ton, and in 1924 they dropped to 6,830 tons, valued at $543,025, or $79.51 a ton. In 1928 they increased again to 9,885 tons, valued at $808,200, or $81.76 per ton.

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Table 7. - Lithopone imported for consumption into the United States, 1913-1928

Year	Quantity short tons	Value	Price per ton
1913	2,363	$146,474	$61.99
1914	3,990	271,310	68,00
1915	2,044	137,816	67.42
1916	2,341	405,730	173.31
1917	224	29,199	130.35
1918	-	-	-
1919	739	122,708	166,05
1920	1,714	263,240	153.58
1921	5,247	432,019	82.34
1922	10,763	885,671	82.29
1923	10,440	776,383	74.37
1924	6,830	543,025	79,51
1925	6,330	478,395	75.58
1926	8,686	661,700	76.18
1927	7,979	656,166	82.24
1928	9,885	808,200	81.76

Prior to 1922 the exports of lithopone from the United States were not separately recorded. Since that year, however, there has been a steady growth in our export trade in this commodity, as is shown in Table 8.

The declared export value per ton has been slightly above that of the domestic sales value and has followed closely the price trend of domestic sales.

Table 8. - Lithopone exported from the United States, 1922-1928.6/

Year	Short tons	Value	
		Total	Average
1922	1,616	$169,982	$105.19
1923	1,485	176,624	118.94
1924	923	104,783	113.52
1925	1,287	132,771	103.16
1926	1,941	200,412	103.25
1927	2,110	222,585	105.49
1928	3,326	337,523	101.48

6/ Not separately recorded prior to 1922.

Correlation of Sales of Barium Pigments With Lead and Zinc Pigments

Barium pigments, especially lithopone, have certain advantages over both white lead and zinc oxide. Lithopone itself is whiter than white lead and equal in whiteness to the best grade of French-process zinc oxide. Unlike

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white lead it is not affected by sulphur or hydrogen sulphide and is nonpoisonous, whereas lead paint is so poisonous that certain countries have prohibited its use for interior decoration. Lithopone does not blacken by combining with lead contained in pigments or driers with which it is mixed. In opacity or drying power it is superior to white lead, and about equal to zinc oxide, but this claim can not be sustained with respect to lithopone when employed in a mixed paint, as the larger quantity of oil used with lithopone reduces the covering power of the paint.

As an exterior paint lithopone is said not to give complete satisfaction when used alone. In direct sunlight it is likely to discolor and turn gray, and its surface becomes chalky and checked. However, the claim is made that by mixing small quantities of other white pigments, such as zinc oxide and whiting (calcium carbonate or chalk) with lithopone, these objections are removed. Such pigments, made in part of lithopone, are on the market and are said to be eminently satisfactory for exterior use. A mixture of 60 per cent of lithopone, 20 per cent of zinc oxide, and 20 per cent of whiting ground in pure linseed oil makes a satisfactory paint for exterior use. Therefore lithopone comes into direct competition with lead and zinc pigments in exterior paint.

Table 9 and figure 2 correlate the sales of barium pigments with the sales of lead and zinc pigments for the years 1910 to 1928.

Table 9. - Barium, lead, and zinc pigments sold by producers in the United States 1910-1928 (in short tons)

Year	Lithopone	Barium sulphate (blanc fixe)	Lead pigments 1/	Zinc pigments 2/
1910	3/ 12,655	(4)	143,810	5/ 50,592
1911	3/ 16,866	(4)	132,612	5/ 46,122
1912	3/ 24,220	(4)	146,833	5/ 64,032
1913	3/ 29,685	(4)	142,626	5/ 70,622
1914	3/ 32,819	(4)	159,474	5/ 70,619
1915	46,494	(4)	156,101	5/ 79,572
1916	51,291	1,229	128,979	5/ 90,276
1917	63,713	3,337	115,200	5/ 97,573
1918	62,403	9,522	102,888	5/ 102,778
1919	78,365	5,227	148,158	145,230
1920	89,373	8,046	158,107	129,904
1921	55,016	2,471	181,851	90,432
1922	83,360	7,349	208,756	148,078
1923	98,199	6,761	174,822	150,491
1924	109,469	7,796	202,066	158,199
1925	145,019	11,748	178,901	183,104
1926	159,931	(6)	162,084	170,782
1927	176,994	13,395	171,177	177,310
1928	200,468	19,081	169,947	185,129

1/ White lead (dry and in oil) and white lead sulphate.
2/ Zinc oxide and leaded zinc oxide.
3/ Marketed production.
4/ Not available.
5/ Zinc content of zinc pigment- domestic and imports.
6/ Bureau of Mines not at liberty to publish figures.

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While the sales of lead pigments have been quite variable over this period, those of zinc and especially of lithopone have shown favorable increases.

The sales of lithopone during the pre-war period (1910 to 1913) averaged 20,856 short tons annually, while during the war period (1914 to 1918) they advanced to an average of 51,344 tons, an increase of 146 per cent. The post-war period sales averaged 119,619 tons annually, an increase of 133 per cent over the war period, and of 474 per cent over the pre-war period.

The sales of lead pigments, while larger, did not show such a tremendous growth. The average sale of lead pigments for the pre-war period (1910 to 1913) was 141,470 tons, or about 7 times that of lithopone for the same period. During the war, however, it decreased, the average being only 132,528 tons, or 6 per cent less than during the previous period. Since the war there has been only a relatively slight increase, the average sale for the years 1919 to 1928 being 175,587 tons, or about 24 per cent more than during the pre-war period.

The sales of zinc pigments, however, have been more favorable. During the pre-war period they averaged 57,842 tons, nearly three times that of lithopone and about one-third that of lead pigments. For the war period they increased to an average of 88,163 tons, or 34 per cent over the previous period, while from 1919 to 1928, inclusive, they averaged 153,866 tons, representing increases of 43 per cent over the war period and of 62 per cent over the pre-war period.

The tremendous growth in the lithopone industry, as compared with its two closest competitors, lead and zinc pigments, augurs well for the future of the industry.

BARIUM CHEMICALS

Preparation

Barium chemicals have important industrial uses in the United States. The most important of these chemicals are as follows: Blanc fixe, or precipitated barium sulphate (which, although practically identical with ground barite in chemical composition, has different physical properties), barium carbonate, chloride, nitrate, hydroxide, and dioxide.

Barium sulphide, which is prepared by heating a mixture of crude barite and some form of carbon (see p. 8), is used as the starting point for the preparation of barium chemicals.

Both barite and witherite are used in the United States as raw material for the manufacture of barium chemicals, but the quantity of the latter consumed for this purpose is relatively small and is largely imported from England. The manufacturers of barium chemicals prefer to use the washed, high-grade barite of the soft type, but they can and do use barite which could not be used in the preparation of the highest grades of ground barite.

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Barium carbonate is precipitated from a solution of barium sulphide by sodium carbonate (soda ash), and sodium sulphide is obtained as a by-product. Barium carbonate can also be prepared by passing a current of carbon dioxide gas through the solution of barium sulphide.

The method of producing blanc fixe or precipitated barium sulphate depends on the physical properties which are desired for the finished product. It was formerly made only by treating a solution of barium chloride with sodium sulphate, or sulphuric acid. It is now usually made by precipitation from a solution of barium sulphide by means of salt cake (sodium sulphate). This method produces a much denser product than that produced from barium chloride and in addition yields sodium sulphide as a valuable by-product. It is also made as a by-product of the manufacture of hydrogen peroxide when barium peroxide is treated with sulphuric acid. For certain color purposes blanc fixe is precipitated from hot, concentrated solutions, thus giving a crystalline product which is a valuable base for the manufacture of very brilliant colors.

Barium chloride may be produced by treating witherite (natural barium carbonate) with hydrochloric acid. It is usually produced in this country directly from crude barite by roasting with coal and calcium chloride. It may also be prepared by treating a solution of barium sulphide with calcium chloride.

Barium nitrate is produced by adding sodium nitrate (Chile saltpeter) either to a solution of barium chloride or to a solution of barium sulphide. It is also produced by dissolving witherite in a solution of nitric acid. The barium nitrate thus produced can be converted into barium oxide, dioxide, or hydroxide.

Barium hydroxide, or caustic barite, is prepared on a large scale by heating barium sulphide in earthenware retorts into which a current of moist carbonic acid is passed, after which superheated steam is passed over the resulting heated carbonate.

Barium peroxide, or dioxide, is prepared from either barium nitrate or barium carbonate. The barium nitrate, or carbonate, is first converted into barium oxide by heating in a closed apparatus, and the barium oxide is then converted into barium peroxide by heating at about 700° C. in a current of air free from carbon dioxide and moisture.

Whenever a sodium salt is added to a solution of barium sulphide in the preparation of barium salts, sodium sulphide is produced as a valuable by-product in addition to the desired barium product. This is an important product of the barium chemical industry, and has a large consumption by the American dye industry in the preparation of sulphur colors, especially sulphur black.

Figure 4 shows the steps, apparatus, and raw materials, used in the manufacture of barium chemicals.

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Uses

Blanc fixe, or permanent white, the precipitated barium sulphate, is the best grade of barium sulphate for pigment purposes, both as to whiteness and fineness of product. It is largely used where a pure white pigment or filler is desired, as in paints, rubber goods, linoleum, oilcloth, and glazed paper. It is also used in lithographic inks and as a base for lake colors. The battleship gray used extensively by the United States Navy contains about 45 per cent of blanc fixe. Under the name of chemically pure barium sulphate it is used as an indicator in X-ray photography.

Blanc fixe is placed on the market in pulp and as a dry powder. The pulp is a paste containing about 30 per cent of water, and is used chiefly by the paper and lithographic ink manufacturers. The dry powder is used for other pigment purposes.

Barium carbonate is a white insoluble salt which finds its largest use in the ceramics industry, where it is employed to prevent scumming on the surface of clay products and for the manufacture of optical glass, for which purpose a chemically pure product is required.

In the past various compounds of barium have been used to prevent the formation of scum, but at present they have practically all been replaced by barium carbonate. Nearly all of the soluble salts which cause this scum are sulphates, and calcium sulphate is by far the most troublesome in this respect. If a sufficient quantity of barium carbonate be added to a clay containing calcium sulphate, the calcium sulphate, which is a relatively soluble salt, will be broken up, but the products of the reaction, - barium sulphate and calcium carbonate, - being relatively insoluble, will not form a scum.

Barium carbonate is also used in growing quantities in the manufacture of flat wall paints. These paints, when containing about 45 per cent of precipitated barium carbonate, produce a velvety finish. Witherite (natural barium carbonate) can not be used for this purpose and should not be confused with precipitated barium carbonate. Barium carbonate is also used as a raw material for making barium peroxide and in the manufacture of certain kinds of enameled ironware.

Barium chloride is a white barium salt which is fairly soluble in water. It crystallizes with two molecules of water and is usually sold in the crystalline or powdered form. It is largely used in the manufacture of blanc fixe, lake colors, and as a mordant for fixing acid dyes on an inert base such as aluminum hydroxide or blanc fixe. Barium chloride is also used in the purification of salt, as a water softener, as a chemical reagent in sulphur determinations, to some extent in the ceramics industry, and in the manufacture of certain photographic chemicals. It has certain medicinal uses.

Barium nitrate is a soluble barium salt used principally for the manufacture of barium peroxide or dioxide. It is also used in pyrotechnics for making green fire and green signal lights and in the manufacture of certain explosives. It also has certain medicinal uses similar to those of barium chloride.

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Barium hydroxide, or caustic barite, has little commercial use in the United States. During periods of high prices for caustic potash, barium hydroxide is used to convert sulphate of potash into caustic potash. It has, until recently, been used in the refining of beet sugar, but as strontium or lime act in similar manner and are not poisonous, they have been substituted, especially the latter, for barium hydroxide. A small quantity, however, is still used in a western sugar refinery for this purpose.

Barium peroxide, or dioxide, finds its only use in this country in the manufacture of peroxide of hydrogen.

Barium monoxide is used for the preparation of barium peroxide, in the manufacture of certain varieties of optical glass, and in Europe in refining beet sugar.

Barium sulphide is the intermediate compound from which the majority of the other barium chemicals are made, and is one of the necessary materials in the manufacture of lithopone. It is also used with lime as a depilatory.

Barium chromate, lemon yellow, or yellow ultramarine, is used as a yellow pigment.

Barium chlorate is used in pyrotechnics and in dyeing.

Barium manganate has been used to some extent as a green pigment.

A mixture of barium sulphate, sulphide and carbonate has been patented by E. E. Fisher (United States Patents 1,665,693 and 1,665,694) for use in mixes for the manufacture of pressed or blown glass ware. This mixture is claimed to be particularly beneficial where sharp corners and intricate patterns have to be completely filled. The barium chemicals used in glass making must be virtually free from iron, silica and dolomite.

Production and Sales

Prior to the World War the United States was almost wholly dependent on imports for its supply of barium chemicals. There was practically no domestic production of the barium salts such as barium dioxide, chloride, nitrate, and blanc fixe. At that time the only chemical product manufactured in this country on a large scale which utilized barite as a raw material was lithopone. The shutting off of imports with the outbreak of the war gave a great stimulus to the establishment of a barium chemical industry in the United States. In addition there were large war demands for certain barium salts (barium peroxide, blanc fixe, and barium nitrate), which greatly increased the domestic production and tended to develop an industry in the United States.

According to Table 10 and figure 1 the use of crude barite for the manufacture of barium chemicals has not shared the increases exhibited in the ground barite or lithopone industries. At no time has the percentage of crude barite used in the chemical industry exceeded 25 per cent of the total used in all industries, and generally it has been much less.

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During the period from 1915 to 1920, inclusive, the barium chemical industry consumed on an average of 24,442 short tons annually of both domestic and imported barite, 18 per cent of that used in all industries.

The average annual consumption of crude barite, both domestic and imported, in the chemical industry during the period from 1921 to 1928, inclusive, was 31,074 tons, an increase of 27 per cent over the preceding period (1915-1920), but only 13 per cent of the total used in all industries.

Table 10. - Crude barite, both domestic and imported, used in the manufacture of barium products, 1915-1928 (in short tons)

Year	Used in barium chemicals	Total used	Per cent of total
1915	10,216	108,622	9
1916	38,283	185,688	20
1917	49,842	196,039	25
1918	38,041	185,763	20
1919	32,976	201,586	16
1920	37,210	229,443	16
1921	10,952	100,607	11
1922	25,303	167,842	15
1923	34,327	210,587	16
1924	33,181	213,163	16
1925	29,141	232,685	13
1926	33,119	281,056	12
1927	34,280	330,190	10
1928	48,289	334,695	14

Tables 11 and 12 show the marketed production of the principal barium chemicals in the United States over a period of years. The total marketed production has registered a steady growth since the world-wide depression year of 1921 and during 1927 and 1928, has exceeded the sales of barium chemicals of any year prior to 1921. The total value has shown an upward trend, although the price per ton has decreased far below that obtaining during and preceding the war.

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Table 11. - Marketed production of barium chemicals 1/ in the United States, 1915-1928, in short tons

Year	Quantity	Value	Price per ton
1915	8,823	(2)	(2)
1916	16,792	$1,962,520	$116.87
1917	22,503	(2)	(2)
1918	23,186	(2)	(2)
1919	20,013	1,519,788	75.94
1920	20,760	1,743,634	83.99
1921	5,487	412,275	75.14
1922	13,901	1,562,216	112.38
1923	16,803	1,231,646	73.30
1924	18,154	1,213,900	66.87
1925	18,654	1,207,770	64.75
1926	21,911	1,325,262	60.48
1927	23,943	1,517,994	63.40
1928	33,969	2,045,156	60.21

1/ Barium chemicals include dioxide, carbonate, chloride, hydroxide, nitrate, sulphate (blanc fixe), and sulphide.
2/ Not available.

Of the barium chemicals sold in the United States, blanc fixe, or precipitated barium sulphate, is by far the most important. During recent years this commodity has accounted for about 33 per cent of the total quantity of the barium chemicals sold. Barium carbonate is the next important of the chemicals and accounts for about 25 per cent of the total.

Table 12. - Barium chemicals sold by producers in the United States, 1918-1928, in short tons

Year	Barium carbonate	Barium chloride	Barium sulphate (blanc fixe)	Other barium chemicals 1/	Total
1918	7,661	4,530	9,522	1,473	23,186
1919	2/ 7,135	4,509	5,227	3,142	20,013
1920	7,484	3,084	8,046	2,146	20,760
1921	1,956	(3)	2,471	1,060	5,487
1922	2,281	2,022	7,349	2,249	13,901
1923	6,362	3,301	6,761	379	16,803
1924	6,058	3,859	7,796	441	18,154
1925	4,962	(3)	11,748	1,944	18,654
1926	5,394	4,592	(3)	11,925	21,911
1927	5,969	3,708	13,395	871	23,943
1928	7,626	5,224	19,081	2,038	33,969

1/ Figures for "other barium chemicals" cover different chemicals for each year.
2/ Figures for 1919 cover production, not sales.
3/ Included under "other barium chemicals."

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Markets and Prices

The barium chemical industry in the United States is well situated as regards markets. The demand for barium chemicals is more limited than that for lithopone or other barium products, and the plants are generally located near their market instead of at the source of raw material, though several are in fairly close promimity to domestic deposits.

The chief markets for barium chemicals are in the East, and the industry comes into direct competition with foreign products, which prior to the war satisfied fully two-thirds of the domestic requirements. The eastern plants are so situated that they are able to use either domestic or imported barite for their needs, and are thus able to furnish their market at the lowest possible price.

The barium chemical industry in the Mid-Western States use the locally produced barite and distribute the finished products to the market areas to the north and west of them.

The western producer of barium chemicals finds his market in the immediate vicinity, and has no competition from either Mid-Western or imported barium chemicals.

The prices of certain barium chemicals are shown in Table 14, for the years 1922 to 1928, inclusive.

Imports and Exports

Table 13 shows the imports for consumption of certain barium chemicals for the years 1902 to 1928, inclusive. There has been a general increase in practically all items, with witherite, blanc fixe, and barium nitrate showing the larger gains. The war curtailed our imports to a great extent, and it was not until 1920 that they returned to anything like the pre-war levels.

Prior to the war practically 90 per cent of the imports of barium chemicals into the United States were represented by three barium salts--namely, precipitated barium carbonate, barium chloride and barium dioxide. Within recent years, however, there has been a considerable growth in the imports of natural barium carbonate, blanc fixe, and barium hydroxide, until they represent nearly one-half of the total imports of barium chemicals.

Previously, these chemicals were generally imported from Germany, but now England, Belgium, and Italy furnish nearly one-half of our import trade in them. Our requirements of witherite, however, are furnished almost solely by England.

It is a question whether the near future will see the same steady growth in the importation of barium chemicals (excepting witherite) as has taken place during recent years. The industry in this country seems now to be on a firm economic and financial basis and able to take care of domestic

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requirements, furnishing the consuming markets with products equally as good and at prices comparable with the imported products. Figure 5 shows the location of barite deposits and barium products plants in the United States.

Table 13. - Value of barium compounds imported into the United States, 1902-1928.

Year	Witherite, barium carbonate		Barium binoxide	Barium chloride	Blanc fixe	Barium nitrate	Barium hydroxide
1902	$12,777		$66,746	$46,905	$25,933	-	-
1903	25,762		84,549	68,762	35,466	-	-
1904	46,133		102,076	43,694	50,901	-	-
1905	45,073		111,856	47,386	53,112	-	-
1906	55,405		152,403	65,242	61,961	-	-
1907	24,552		167,519	79,333	85,713	-	-
1908	22,159		181,533	42,291	73,131	-	-
1909	31,584		255,013	47,352	65,427	-	-
1910	25,229		341,631	35,614	67,975	-	-
1911	27,351		270,917	28,896	71,049	-	-
(1)	Natural	"Precipitated barium carbonate"					
1912	$15,777	$ 9,938	252,320	27,655	70,327	-	-
1913	13,116	38,949	239,000	37,620	62,785	-	-
1914	8,084	28,221	332,709	68,866	32,619	-	-
1915	12,165	2,786	218,776	31,295	18,501	-	-
1916	18,169	-	6,590	608	17,810	-	-
1917	17,321	1,554	-	-	3,333	-	-
1918	14,134	-	-	-	-	-	-
1919	4,739	2,666	-	19,846	90	-	-
1920	61,284	37,462	64,447	151,778	8,485	-	-
1921	25,188	80,603	127,631	72,621	22,470	-	-
1922	39,114	210,250	189,334	112,785	76,445	$16,795 2/	$6,573 2/
1923	41,823	79,482	152,270	75,014	32,063	59,766	16,872
1924	56,415	128,217	120,374	100,810	50,465	54,638	8,241
1925	63,634	160,164	70,553	67,306	81,439	58,192	5,605
1926	80,679	189,167	8,157	49,426	136,697	49,494	9,789
1927	65,821	119,014	1,264	45,285	107,179	65,284	12,439
1928	82,434	116,241	1,310	25,253	168,923	69,010	10,031

1/ Figures prior to 1912 included both "natural" and "precipitated barium carbonate."

2/ Not separately recorded prior to the tariff of Sept. 22, 1922.

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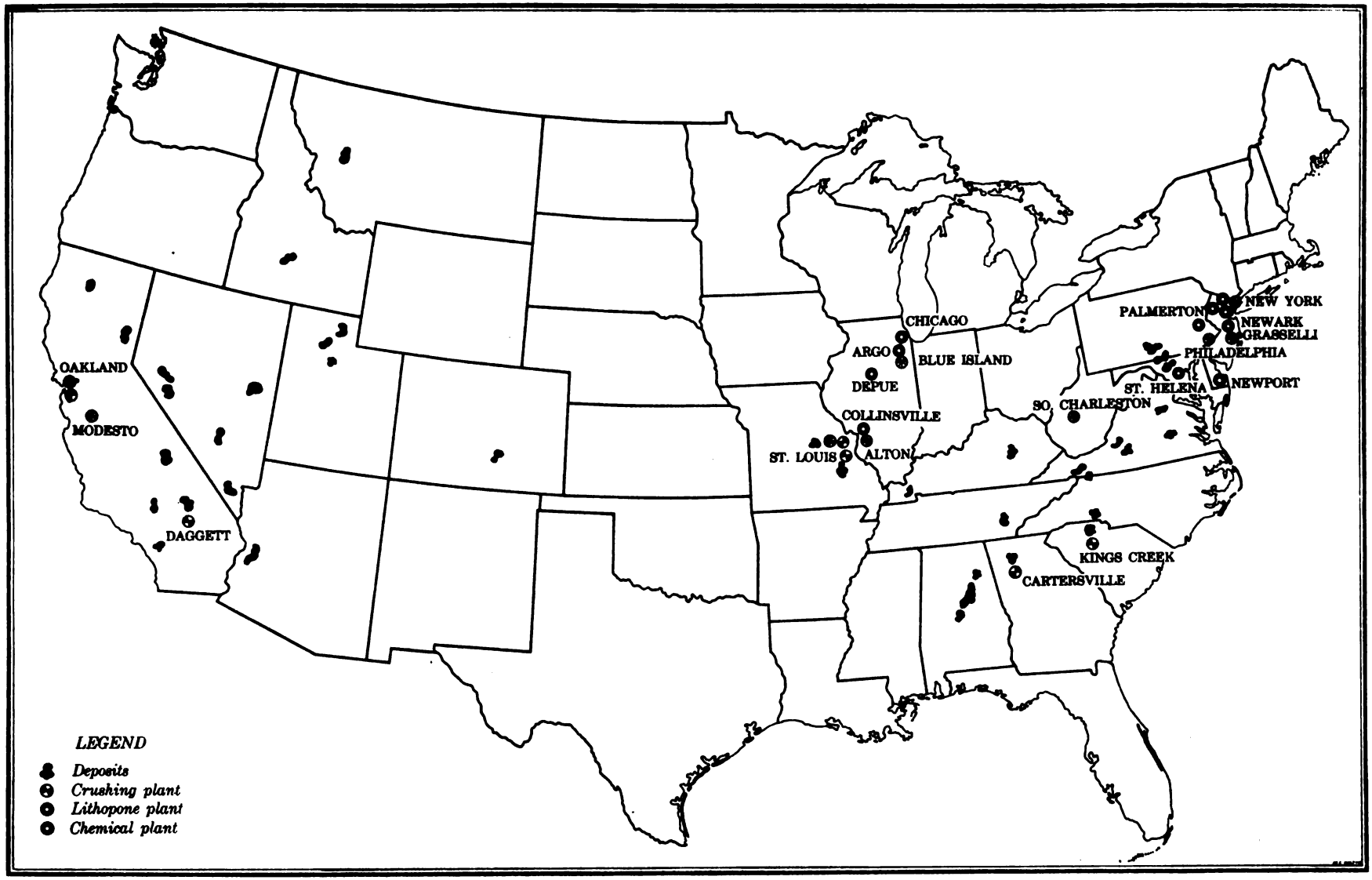

Figure 5. – Location of barite deposits and barium products plants

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Table 14. - Prices of barite and barium products 1/

		1922	1923	1924	1925	1926	1927	1928
Barite, crude (short ton)	High	$ 7.25	$ 7.77	$ 9.00	$8.50	$8.50	$8.00	$7.50
	Low			8.00		8.00		6.50
Barite, ground (short ton)	High	26.00	28.00	26.00	23.00	23.00	23.00	23.00
	Low	23.00	25.00	22.00	22.000			
Blanc fixe (dry) (pound)	High	.04¼	.04¼	.05	.05	.04½	.04 3/8	.04½
	Low			.04	.04	.04	.04¼	.03 5/8
Blanc fixe(pulp) (short ton)	High	50.00	60.00	70.00	70.00	65.00	65.00	$60.00
	Low	40.00	40.00	50.00	55.00	53.00	60.00	40.00
Barium carbonate (short ton)	High	85.00	90.00	90.00	65.00	55.00	54.00	60.00
	Low	48.00	66.00	63.00	54.00	50.00	48.00	47.50
Barium chlorate (pound)	High	.45	.15	.15	.15	.15	.15	.15
	Low	.14	.14	.14	.14	.14	.14	.14
Barium chloride (short ton)	High	115.00	100.00	95.00	72.50	66.00	65.00	$70.00
	Low	50.00	80.00	70.00	60.00	60.00	52.00	54.00
Barium nitrate (pound)	High	.10¼	.10¼	.10	.09	.09	.10	.08½
	Low	.06	.07½	.08	.08	.07½	.07½	.08¼
Lithopone (pound)	High	.06¼	.07¼	.08 5/8	.06 5/8	.06 5/8	.05 7/8	.05 7/8
	Low	.06	.06	.06 3/8	.06 1/8	.05 7/8		.05¾

1/ Quotations on crude and ground barite are taken from Engineering and Mining Journal Press. Other quotations from Oil, Paint and Drug Reporter. The following are the designations, on which quotations in the preceding table are based:-

Crude barite, "f.o.b. mines."
Ground barite, "domestic, including barrels, f.o.b., St. Louis."
Lithopone, "in barrels, l.c.l."
Barium carbonate, "bags, works."
Barium chlorate, "kegs."
Barium chloride, "crystals, bags."
Barium nitrate, "casks."
Barium sulphate (blanc fixe), "dry, in barrels, l.c.l."
Barium sulphate (blanc fixe), "pulp works."

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The following is a list of producers of ground barite and barium products:

GROUND BARITE

Name and Address of Company	Location of Plant
Chemical & Pigment Co. (Inc.), Oakland, Calif.	Oakland, Calif.
Clinchfield Sand & Feldspar Co., Baltimore, Md.	Kings Creek, S. C.
C. P. DeLore Co., St. Louis, Mo.	Miss. River & River Des Peres, St. Louis, Mo.
Flynt Silica & Spar Co., Los Angeles, Calif.	Daggett, Calif.
National Pigments & Chemical Co., St. Louis, Mo.	St. Louis, Mo.
Thompson, Weinman & Co., New York, N. Y.	Cartersville, Ga.

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LITHOPONE

Name and Address of Company	Location of Plant
Chemical & Pigment Co. (Inc.), Oakland, Calif.	Oakland, Calif.
Chemical & Pigment Co. (Inc.), Oakland, Calif.	Collinsville, Ill.
Chemical & Pigment Co. (Inc.), Oakland, Calif.	St. Helena, Md.
E. I. du Pont de Nemours & Co., Wilmington, Del.	Newark, N. J.
E. I. du Pont de Nemours & Co., Wilmington, Del.	Philadelphia, Pa.
Eagle-Picher Lead Co., Chicago, Ill.	Argo, Ill.
Grasselli Chemical Co., Cleveland, Ohio.	Grasselli, N. J.
Krebs Pigment & Chemical Co., Newport, Del.	Newport, Del.
Mineral Paint Zinc Co., New York, N. Y.	Depue, Ill.
New Jersey Zinc Co. (of Pennsylvania), New York, N. Y.	Palmerton, Pa. (2 plants)
Sherwin-Williams, Cleveland, Ohio.	Chicago, Ill.
United Color & Pigment Co., Newark, N. J.	Newark, N. J.

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BARIUM CHEMICALS[5/]

Name and Address of Company	Location of Plant
Alton Barium Products Co., Alton, Ill.	Alton, Ill.
Barium Products (Inc.), Modesto, Calif.	Modesto, Calif.
Barium Reduction Corporation, Charleston, W. Va.	So. Charleston, W. Va.
Chicago Copper & Chemical Co., Chicago, Ill.	Blue Island, Ill.
E. I. du Pont de Nemours & Co., Wilmington, Del.	Philadelphia, Pa.
Grasselli Chemical Co., Cleveland, Ohio.	Grasselli, N. J.
Oakland Chemical Co., New York, N. Y.	New York, N. Y.
Titanium Pigment Co. (Inc.), New York, N. Y.	Carondelet Station, St. Louis, Mo.

5/ Includes only those using barite.

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I. C. 6223 (REVISED)

FEBRUARY, 1930

DEPARTMENT OF COMMERCE

UNITED STATES BUREAU OF MINES
SCOTT TURNER, DIRECTOR

INFORMATION CIRCULAR

BARITE AND BARIUM PRODUCTS

PART II. BARIUM PRODUCTS

BY

R. M. SANTMYERS

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(Revised)

February, 1930.

INFORMATION CIRCULAR

DEPARTMENT OF COMMERCE - BUREAU OF MINES

BARITE AND BARIUM PRODUCTS[1]

Part II. Barium Products

By R. M. Santmyers[2]

CONTENTS

	Page
Introduction	2
Ground barite	3
Preparation	3
Uses	3
Production	4
Market and prices	5
Imports and exports	7
Lithopone	8
Preparation	8
Use	9
Production and sales	10
Market and prices	11
Imports and exports	12
Correlation of sales of barium pigments with lead and zinc pigments	13
Barium chemicals	15
Preparation	15
Uses	17
Production and sales	18
Market and prices	21
Imports and exports	21

1/ The Bureau of Mines will welcome reprinting of this paper, provided the following footnote acknowledgment is used: "Reprinted from U. S. Bureau of Mines Information Circular 6223."

2/ Mineral specialist, rare metals and nonmetals division, U. S. Bureau of Mines.

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INTRODUCTION

Barium is derived from two minerals, barite (barium sulphate) and witherite (barium carbonate). Metallic barium is at present of little commercial importance, although small quantities are used as a scavenger of gases in the manufacture of radio tubes and as a hardening agent for lead; however, barium compounds, many of which are manufactured from the minerals by chemical processes, constitute an important class of commercial products and enter into both domestic and foreign trade in considerable quantities.

Barium products may be roughly divided into three classes: (1) Ground barite; (2) lithopone; and (3) barium chemicals. Ground barite - crude ore which has been washed, jigged, and ground very fine - is used as a filler in numerous substances, such as paper, paints, rubber, etc., where a heavy, chemically inert substance is required. Lithopone - a mixture of approximately 70 per cent barium sulphate, 26 to 28 per cent of zinc sulphide and 1 to 3 per cent of zinc oxide - is a widely used white pigment. Barium chemicals find employment in a wide variety of industries. The manufacture of lithopone, at present, consumes by far the larger part of the crude barite produced and imported into this country and has expanded rapidly in recent years. Prior to the war the entire lithopone industry of the United States was located along the Atlantic coast practically at tidewater. The barite required by the industry was supplied by imports, chiefly from Germany, as the imported material cost less than domestic barite. War conditions forced lithopone manufacturers to develop deposits in Georgia, Tennessee, South Carolina, and elsewhere in the Southern States in order to obtain supplies of raw material. At the same time the manufacture of lithopone was started in the Middle West, utilizing crude barite from Missouri. With the termination of the war and the reappearance of German barite on the American market, the Southern field is finding it more and more difficult to furnish the eastern lithopone industry with crude ore.

The list of commercial barium chemicals includes blanc fixe or artificial sulphate of barium, barium carbonate, chloride, nitrate, monoxide, dioxide, hydroxide, sulphide, chlorate, and chromate. A few of these chemicals, however, are of only small importance. Barium sulphide (an intermediate product from which the majority of the other barium chemicals are made), blanc fixe and barium dioxide, chloride, nitrate, carbonate and hydroxide are the barium chemicals that are used extensively.

Prior to the war the United States was wholly dependent on imports for its supply of barium chemicals. Germany was the largest producer and furnished about two-thirds of the domestic requirements. Between 80 and 90 per cent of the imports were represented by three barium salts - barium carbonate, barium chloride, and barium dioxide. The cessation of imports and the war demand for barium chemicals (barium nitrate, blanc fixe, and barium dioxide) resulted in the establishment of a barium chemical industry in this country.

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Domestic plants were erected chiefly in the East and Southeast, although there were plants in Ohio and Illinois. In some cases the plants were located relatively close to the domestic deposits of barite. The chief markets for barium chemicals were in the East, and upon the termination of the war domestic products came into direct competition with imported chemicals. The eastern plants are so situated that they can use either imported or domestic barite as raw material, and therefore are able to compete with imported barium chemicals.

Those plants located close to the southern barite deposits and those in the Middle West depend solely on domestic crude barite which costs more than that imported from Germany. In these areas the higher cost of raw materials, however, is partly offset by the fact that although barium chemicals are not particularly bulky, differences in freight rates tend to equalize the final costs of the domestic and foreign products.

GROUND BARITE

Preparation

The preparation of ground barite varies in different plants and according to the condition of the ore. The general practice, however, is to crush the ore to about 1 inch and by log washing to remove the clay and earthy material. Often this washing is done at the mine and need not be repeated at the grinding mill. The next step is to grind the cleaned material, usually in tube mills; then the ground barite, suspended in water, is either screened or water floated in order to remove any coarse particles. If off-color, the finely ground barite is bleached with sulphuric acid, which removes the stains due to oxides of iron. After being washed several times with water, the bleached product is dried, pulverized, and packed in bags or barrels. Very little labor is required in the process of grinding after the ore is placed in the first or primary crusher until it reaches the packing room. The barite is conveyed mechanically or pumped, suspended in water, through the different processes.

Uses

The principal use of ground barite is as a filler. Since it is extremely heavy, chemically inert and white, it is admirably fitted for this purpose. The paint, paper, rubber, linoleum, and cloth industries all use considerable quantities to add weight and body to their products. By far the larger part - estimated at 50 to 70 per cent - of all the ground barite produced and sold in the United States is consumed in the paper and rubber industries.

As a rubber filler, bleached or unbleached, ground barite is employed where a soft rubber article is desired, as in rubber bands, tubing and the like, but not where strength and resistance to abrasion is required, as in auto tires. The bleached form is used in papers where weight is desirable with a high finish, as in Bristol board, playing cards, and plate paper. Natural barite is not often used in high-grade paints, but a limited quantity is employed in the cheaper grades and a small amount of the bleached mineral is used directly as an extender and loader and as a base for lake colors.

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Finely ground barite mixed with a colloidal clay, such as bentonite, and a suitable suspending medium is effective in making up heavy liquids used as a seal in drilling for oil and gases. The heavy liquid holds back the gas flow until the casing can be placed. Finely divided iron oxide in suspension is employed for the same purpose.

A limited amount of unbleached ground barite is used in molded goods, such as buttons and hard rubber articles. One of its newer uses in the molded hard-rubber industry is as a component part of the protecting hard-rubber shield around X-ray tubes. Because of its high density, ground barite tends to absorb the rays and thereby protect the operator, except where the shield is open. Plaster containing a large admixture of ground barite is used on walls of X-ray rooms in order to limit the radiation of the rays. It is also used in making brick for the construction of X-ray laboratories, replacing in both cases the lining of sheet lead used to prevent the rays from escaping and doing possible injury.

Barium platino-cyanide has the property of becoming fluorescent under the action of X-rays and ultra-violet light rays. This barium compound is used in X-ray photography by coating the projecting screen with it. The shadows made by the rays are thus outlined on the screen.

A small quantity of ground barite is used in the manufacture of artificial ivory. Some barite is used as a flux in brass smelting, and is also used in the extraction of iron in reclaiming brass from junk.

Production

The production of ground barite has increased during recent years, but not as rapidly as the production of crude barite. During the years 1915 to 1920 from 31 to 50 per cent of the crude ore consumed in all industries was used for the manufacture of ground barite, but during the years 1921 to 1928 the proportion was only 20 to 29 per cent of the total. This decrease in the percentage of crude barite used for grinding is not due to any great extent to an increase in the imports of ground barite, but to a tremendous growth that that has taken place in the lithopone industry since 1922.

Table 1 and figure 1 show the amount of crude barite used in the manufacture of ground barite, and the percentage of the total for the years 1915 to 1928:

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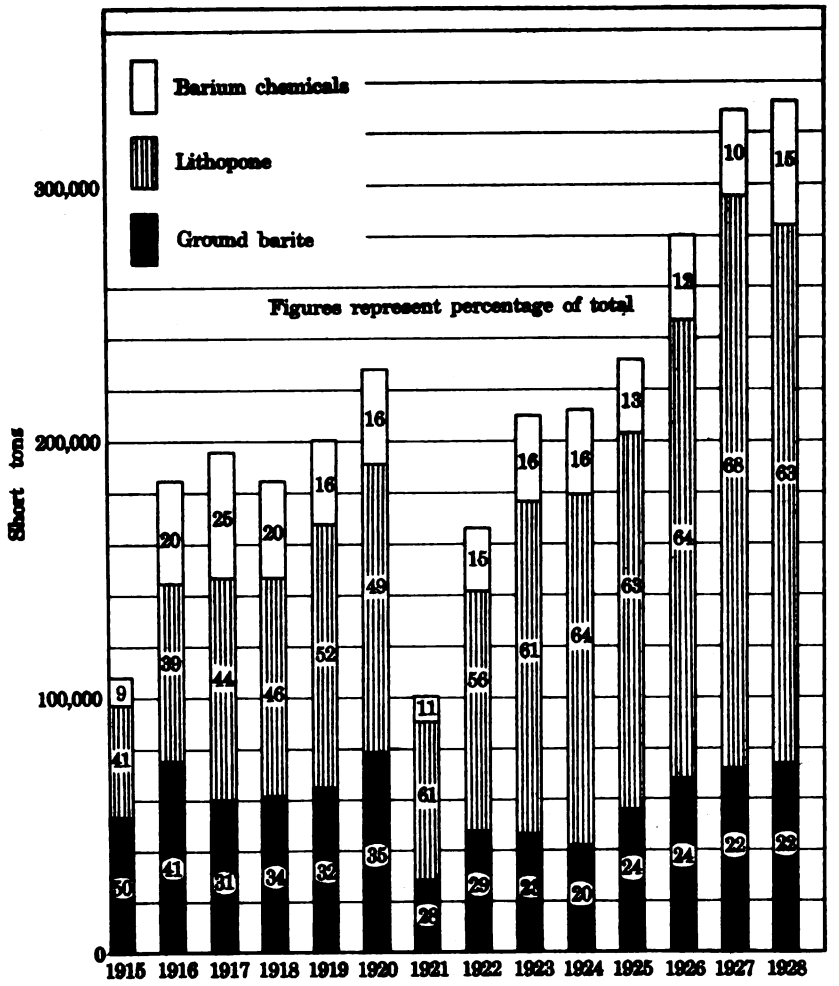

Figure 1. – Crude barite used in the manufacture of barium products

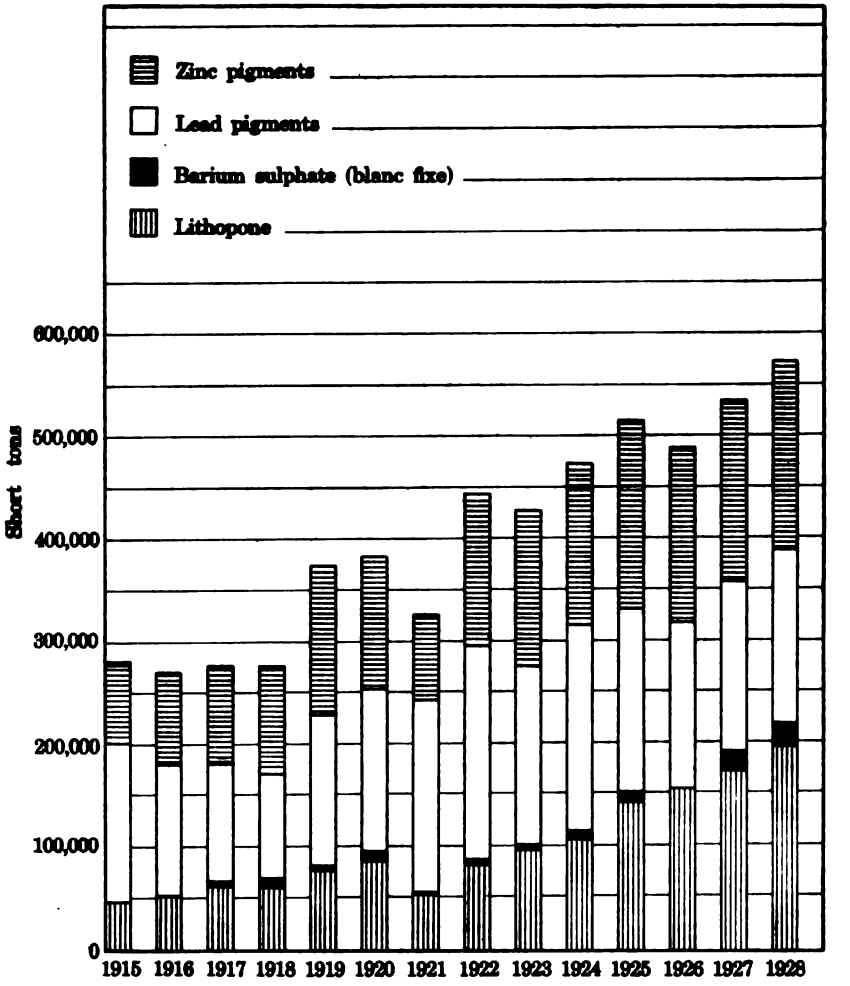

Figure 2. – Sales of barium, lead, and zinc pigments

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Table 1. - Crude barites, both domestic and imported, used in the manufacture of barium products, 1915-1928 (in short tons)

Year	Used for grinding	Total used	Per cent of total
1915	53,903	108,622	50
1916	75,507	185,688	41
1917	60,132	196,039	31
1918	62,440	185,763	34
1919	64,922	201,586	32
1920	79,052	229,443	35
1921	28,296	100,607	28
1922	48,280	167,842	29
1923	47,713	210,587	23
1924	42,855	213,163	20
1925	56,851	232,685	24
1926	69,048	281,056	24
1927	73,119	330,190	22
1928	74,814	334,695	22

The grinding of barite is carried on chiefly in Missouri, which in recent years has produced 80 to 85 per cent of the barite ground in the United States from domestic ore. The other States which produce ground barite are Georgia, 5 to 6 per cent of the total; California, 4 to 6 per cent; and South Carolina, 6 to 8 per cent.

The dominant position held by Missouri in the ground barite industry is due to the grade and texture of the ore which is soft and easy to grind as compared with the hard crystalline variety found in other sections of the country.

Market and Prices

The market for ground barite is divided about equally between the Mid-Western field (St. Louis to Chicago) and the Atlantic Coast States. About 50 per cent of the ground barite used in the eastern market is supplied from Missouri, and the remainder is obtained in part from the Southern field and in part from imports (chiefly from Germany).

The principal rubber manufacturers who use ground barite as a filler in their products are located in and around Akron, Ohio, and in the vicinity of New York City. Most of the ground barite used by these companies is from Missouri, as the Southern ore enters into the rubber industry in only small quantities.

The paint industry, on the other hand, although it is located in practically the same two districts as the rubber industry, also includes Michigan, Illinois, and Indiana in the mid-western market, and Pennsylvania and Delaware in the eastern market. Though Missouri furnishes the paint industry with the larger part of its barite requirements, a greater proportion of Southern ore is used in this industry than in the rubber industry.

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The price of ground barite has remained almost stationary in recent years; the average annual price as reported by producers to the Bureau of Mines ranges between $20 and $22 per short ton. Prior to the war the price ranged from $11.19 per ton in 1908 to $14.18 in 1913, and when hostilities began the price dropped to $12.95 in 1914 and then to $12.32 in 1915, but immediately advanced until in 1918 it reached $18.91 per ton.

Table 2. - Ground barite sold by producers in the United States,[1] 1908-1928

Year	Quantity short tons	Value	Average price
1908 [2]	28,415	$ 318,096	$11.19
1909 [2]	34,673	455,506	13.14
1910 [2]	38,165	475,001	12.45
1911 [2]	39,611	503,867	12.72
1912 [2]	38,225	495,895	12.97
1913 [2]	37,033	525,300	14.18
1914 [2]	35,815	463,858	12.95
1915 [2]	51,557	635,318	12.32
1916	65,440	964,802	14.74
1917	52,694	951,220	18.05
1918	55,086	1,041,608	18.91
1919	[3] 57,985	1,163,437	20.06
1920	65,748	1,381,868	21.02
1921	27,661	622,871	22.52
1922	46.176	933,722	20.22
1923	39,605	895,095	22.60
1924	38,296	784,881	20.50
1925	49.674	1,040,461	20.95
1926	57,812	1,186,563	20.52
1927	57,658	1,166,294	20.23
1928	64,425	1,332,228	20.68

1/ From domestic and imported ore.
2/ Sales of refined barite (domestic only).
3/ Figures cover production, not sales (1919).

Table 3 shows the prices of ground barite per long ton, washed and water floated, f. o. b. plants, bags extra, as quoted from the Engineering and Mining Journal.

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Table 3. - Prices of Ground Barite (Washed and Water floated, f.o.b. mines, bags extra) for Georgia and Missouri, by year, each month.

	Georgia		Missouri					
	1928	1929	1924	1925	1926	1927	1928	1929
Jan.		$19.00	$26 $28	$23 $24	$23	$23	$23	$23
Feb.		$19.00	$23 $24	$23 $24	$23	$23	$23	$23
Mch.	$19.00	$19.00	$23 $25	$23 $24	$23	$23	$23	$23
Apr.	$19.00	$19.00	$23 $25	$23 $24	$23	$23	$23	$23
May	$19.00	$19.00	$23 $24	$23 $24	$23	$23	$23	$23
June	$19.00	$19.00	$23 $24	$23 $24	$23	$23	$23	$23
July	$19.00	$19.00	$23 $24	$23 $24	$23	$23	$23	$23
Aug.	$19.00	$18.00	$23 $24	$23 $24	$23	$23	$23	$23
Sept.	$19.00	$18.00	$23 $24	$23 $25	$23	$23	$23	$23
Oct.	$19.00		$23 $24	$23 $24	$23	$23	$23	
Nov.	$19.00		$23 $24	$23 $24	$23	$23	$23	
Dec.	$19.00		$23 $24	$23 $24	$23	$23	$23	
Average:	$19.00		$23.88	$23.58	$23	$23	$23	
High	$19.00	$19.00	$28.00	$24.00	$23.00	$23.00	$23.00	
Low	$19.00	$19.00	$23.00	$23.00	$23.00	$23.00	$23.00	

IMPORTS AND EXPORTS

The following Table No. 4 shows the imports of ground barite for consumption for the years 1910 to 1928, inclusive.

The imports of ground barite, though formerly important, now play only a small part in the ground barite industry of the United States. Since 1923 they have never exceeded 3,000 tons in any one year. The declared value per ton, as reported in the statistics, plus freight, duty and other charges, indicates that the apparent delivered cost is as high, or higher, than the price obtained for the domestic product.

As previously stated, about 50 per cent of the production of ground barite is consumed along the Atlantic seaboard where it comes in direct competition with German ground barite, but due to the careful preparation of the domestic product as regards fineness, uniformity of quality, etc., and the fact that shipments are made promptly from stocks at American mills, Germany has failed to obtain as strong a foothold in the ground barite industry as it has in the case of crude barite.

There are no recorded exports of ground barite, though it is understood that small quantities are shipped to paint, paper and rubber plants in Canada.

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Table 4. - Imports of ground barite for consumption in the United States, 1910-1928

Year	Rate of duty	Quantity short tons	Value	Price per ton
1910	$5.25 per ton	3,023	$ 27,191	$ 8.99
1911	do	3,655	26,462	7.24
1912	do	3,012	21,642	7.19
1913	do	5,145	36,819	7.16
1914 1/	do	1,107	7,520	6.79
1914 2/	20 per cent ad va-	4,919	35,105	7.14
1915	do lorem	1,966	14,997	7.63
1916	do	-	2	-
1917	do	235	3,813	16.23
1918	do	-	-	-
1919	do	-	-	-
1920	do	274	3,017	11.01
1921	do	1,002	16,942	16.91
1922 3/	do	3,027	43,392	14.34
1922 4/	$7.50 per ton	1,166	16,061	13.77
1923	do	6,022	88,741	14.71
1924	do	2,830	38,292	13.53
1925	do	3,203	40,008	12.49
1926	do	3,347	44,781	13.38
1927	do	3,259	38,568	11.83
1928	do	3,089	33,378	10.80

1/ From July 1 to Oct. 3, 1913.
2/ From Oct. 4, 1913 to June 30, 1914.
3/ From Jan. 1, 1922, to Sept. 21, 1922.
4/ From Sept. 22 to Dec. 31, 1922.

LITHOPONE

Preparation

The basic raw materials necessary for the manufacture of lithopone are crude barite; coal, coke, or petroleum breeze; zinc; and sulphuric acid. Other chemicals, such as ferric oxide, alumina, lime, and magnesia are required in the process of manufacture, but in minor quantities. Large quantities of clean, soft water are required in making up solutions and in the washing of lithopone to remove soluble impurities. The manufacture of lithopone requires the preliminary production of a solution of barium sulphide and a solution of zinc sulphate. For the preparation of barium sulphide, the crude barite is first crushed and mixed with the proper proportions of pulverized coal or other forms of carbon. This proportion varies slightly with individual manufacturers; it is generally one part of coal to four parts of barite by weight. After heating the mixture for about four hours in a rotating furnace, the barium sulphate is reduced to barium sulphide. The crude sulphide (black ash), which contains about 70 per cent barium sulphide, is then treated with hot water, and the resulting solution of barium sulphide is clarified.

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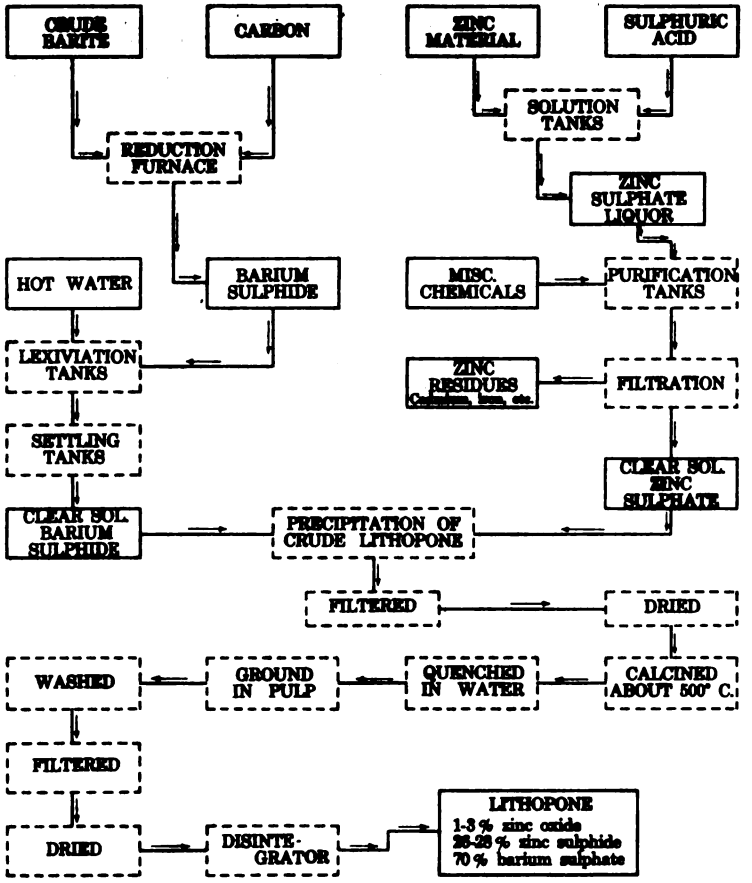
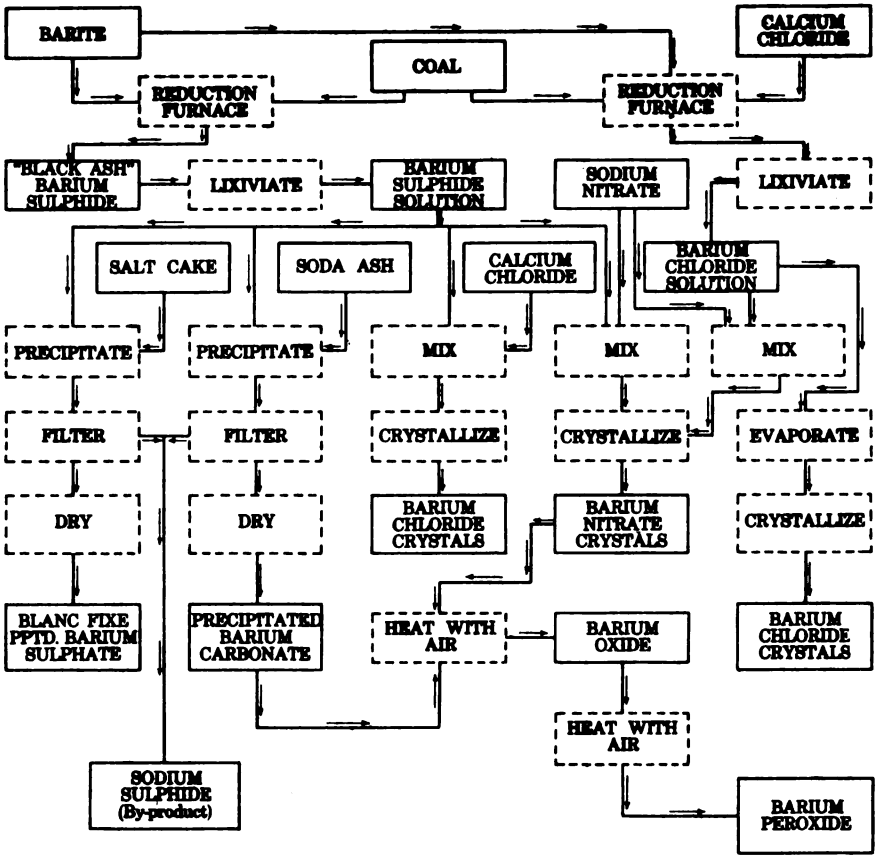


LEGEND
Solid lines.----Raw, intermediate, or finished products
Broken lines.--Apparatus, or steps in process

Figure 3. – Flow sheet for the manufacture of lithopone



LEGEND
Solid lines.----Raw, intermediate, or finished products
Broken lines.--Apparatus, or steps in process

Figure 4. – Flow sheet of the barium chemical industry

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The zinc sulphate solution is prepared by dissolving zinc--in the form of zinc ash, scrap, skimmings, slab zinc, or roasted ore--in dilute sulphuric acid. Since the zinc materials usually contain as impurities other metals (iron, copper or cadmium) which would form colored products on treatment with barium sulphide, the zinc sulphate solution must be purified. Various chemicals are used for this purpose, and this purification, since it represents one of the most important steps in the entire process of manufacture, requires careful chemical control.

Crude lithopone is precipitated from the purified zinc sulphate solution as a white insoluble substance by adding a hot solution of barium sulphide. The crude lithopone is filtered off, dried, and then calcined at 700 to 900 degrees C., with exclusion of air. Waste heat from the barite reduction furnace may or may not be utilized in the calcining furnace. The hot lithopone is thrown into water, ground, washed several times with water to remove soluble impurities, filtered, and dried. After being run through a disintegrator and reduced to a fine powder, the dry product is packed in bags or barrels for shipment. In some cases the lithopone is air-floated to insure a uniform product. The process is shown graphically in Figure 3.

There is very little variation in the composition of domestic lithopones today. The zinc sulphide content in all cases is approximately 28.5 per cent, excepting so-called "high strength" lithopones, which are a distinctive product produced in small quantities and sold under special trade names.

The following is representative of the commercial American product:-4/

$BaSO_4$	71.0
ZnS	28.5
ZnO	.3
Not reported	.2
	100.0

Inferior qualities sometimes contain natural barite which reduces the opacity and covering power and causes them to give a yellowish-white tint when used in linoleum. The natural mineral may be detected by means of the microscope, the precipitated barium sulphate appearing as a fine powder composed of minute crystals of uniform size, whereas the natural barite consists of transparent irregular fragments of larger size. In addition to purity, the value of a particular brand of lithopone is affected by its fineness, whiteness, resistance to light, opacity and uniformity.

Uses

While lithopone was not produced in the United States prior to 1906, its use has grown tremendously in recent years, due to its excellent qualities as a pigment in paints for both interior and exterior use. On account of its whitening properties, it is also used in large quantities as a pigment in rubber goods, paper, linoleum, oilcloth and in window-shade cloth.

4/ Conover, J. D., (Sec't. American Zinc Inst.) Letter dated November 4, 1930.

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The use of lithopone was limited at first to interior paints. But in 1920, after considerable research a lithopone pigment was produced which was sufficiently resistant to sunlight and moisture to permit its being used in exterior paints. This marked the beginning of the great growth in the production of lithopone in the United States.

The following Table 4-A shows the distribution of lithopone sales by consuming industries for the past three years. The paint, varnish and lacquer industries consume by far the larger part of the lithopone sold. For the years 1927 to 1929, inclusive, these three industries consumed approximately 74 per cent of the total sales of lithopone. The floor coverings and textiles industries (linoleum, oilcloth, shadecloth, etc.) consumed between 17 and 18 per cent of the total sales of lithopone, while the rubber industry used between 3 and 4 per cent. All other industries consumed the balance or from 4 to 5 per cent.

Production and Sales

The rapid growth during recent years in the output of crude barite was the direct result of a remarkable and rapidly increasing demand for lithopone as a paint pigment.

Table 5 shows the amount of crude barite used in the manufacture of lithopone and the ratio of this consumption to the total barite used in all industries for the years 1915 to 1928, inclusive.

Up to and including the war period the amount of crude barite used for the manufacture of lithopone never exceeded 50,000 short tons annually, while the percentage consumed in this industry never exceeded 46 per cent. Since the war, however, the tonnage of crude barite sold for this use increased rapidly until in 1928, 211,592 short tons were consumed. The percentage of the total consumed in all industries likewise advanced rapidly, until in 1927 68 per cent of the total sales of crude barite were used in the manufacture of lithopone (63 per cent in 1928).

Table 5. - Crude barite, both domestic and imported, used in the manufacture of barium products, 1915-1928 (in short tons)

Year	Used in lithopone	Total used	Per cent of total
1915	44,503	108,622	41
1916	71,898	185,638	39
1917	86,065	196,039	44
1918	85,282	185,763	46
1919	103,688	201,586	52
1920	113,181	229,443	49
1921	61,359	100,607	61
1922	94,259	167,842	56
1923	128,547	210,587	61
1924	137,127	213,163	64
1925	146,693	232,685	63
1926	178,889	281,056	64
1927	222,791	330,190	68
1928	211,592	334,695	63

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The marketed production of lithopone has followed closely the sales of crude barite to the lithopone manufacturers, the sales totalling 8,000 to 10,000 tons less annually than that reported as consumed for its manufacture. As may be seen in Table 6, the marketed production prior to the war never exceeded 30,000 short tons, the average for the years 1910 to 1913 being 20,856 short tons. During the war period (1914 to 1918) the production increased rapidly, due to the growing demand and the discontinuance of lithopone imports.

Table 4-A. - Distribution of lithopone sales by industries, 1927, 1928, and 1929.

	1927		1928		1929	
	Short tons	Per cent	Short tons	Per cent	Short tons	Per cent
Paints, varnish, lacquers	131,145	74.1	149,122	74.4	150,804	73.1
Floor coverings and textiles	31,186	17.6	35,416	17.7	37,506	18.2
Rubber	7,653	4.3	6,898	3.4	7,176	3.5
Other uses	7,010	4.0	9,032	4.5	10,829	5.2
	176,994	100.0	200,468	100.0	206,315	100.0

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The average for this five-year period was 51,344 tons, an increase of 146 per cent over the pre-war period. Following the war, the marketed production fluctuated considerably until after the general depression year 1921, when production returned to its normal growth. The average production for this period (1919 to 1928) increased to 119,619 short tons, an increase of 133 per cent over the pre-war period.

The price per ton obtained for lithopone on the American market advanced rapidly with the advent of war until in 1920, the all-time high price of $139.69 per ton was reached. Since then, however, the price has again fallen to a normal increase over that of the pre-war period, the price in 1928 reaching $95.15 per ton.

Table 6. - Marketed production of lithopone, 1910-1928, in short tons

Year	Quantity	Value	Price per ton
1910	12,655	$ 916,512	$ 72.42
1911	16,866	1,243,108	73.70
1912	24,220	1,702,119	70.28
1913	29,685	2,170,445	73.12
1914	32,819	2,490,530	75.89
1915	46,494	3,760,472	80.88
1916	51,291	5,798,927	113.06
1917	63,713	7,406,896	116.25
1918	62,403	7,923,276	126.97
1919	78,365	10,218,850	130.40
1920	89,373	12,484,925	139.69
1921	55,016	6,281,563	121.45
1922	83,360	9,214,040	110.53
1923	98,199	11,608,443	118.21
1924	109,469	12,531,397	114.47
1925	145,019	15,186,147	104.72
1926	159,931	16,062,197	100.43
1927	176,994	17,163,620	96.97
1928	200,468	19,073,914	95.15

Market and Prices

The demand for lithopone, though well distributed throughout the United States, is concentrated chiefly along the Atlantic seaboard, in the Middle-Western States (from St. Louis to Chicago), and in the Pacific Coast States, principally California and Washington.

Prior to the war the lithopone requirements of the United States were furnished almost solely by eastern plants using both domestic and imported crude barite. The imported ore, however, was delivered to consumers at a price much lower than that of the domestic material. Before the war Missouri was the principal source for crude ore for lithopone requirements in the East, which necessitated a long freight haul to the lithopone plants on the Atlantic seaboard.

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With the advent of war, crude barite imports ceased, and the eastern manufacturers of lithopone, in order to secure a source of raw material, developed the barite deposits in the Southern States, principally those in Georgia, Tennessee, and Kentucky.

Later, in order to meet the growing demand for lithopone in the Mid-Western States, eastern paint manufacturers constructed plants at St. Louis, Mo., and in neighboring States, utilizing locally produced crude barite. This new industry expanded rapidly and with the termination of the war was able to hold its own in seeking an outlet for its finished product.

About 1926 the lithopone industry was started in California using locally produced barite, and as the industry did not meet with competition from either the Missouri or eastern products it prospered.

Table 14 shows the prices obtaining for lithopone for the years 1922 to 1928, as quoted by the Oil, Paint and Drug Reporter. A slight decrease is noticeable during this period. In 1922 the price ranged from 6 to 6¼ cents per pound, f. o. b. New York, and represented a slight decline from the prices quoted in the preceding year. In 1923 and again in 1924, there were marked advances, the price ranging from 6 to 7¼ cents per pound during the former year, and from 6-3/8 to 8-5/8 cents during the latter year. In 1925, however, quotations dropped to 6-1/8 to 6-5/8 cents, and in 1928 the prices ranged from 5-3/4 to 5-7/8 cents, the lowest price for this product over a range of 10 years.

Imports and Exports

The imports of lithopone into the United States have never exceeded 11,000 short tons a year.

Table 7 shows the tonnage, the declared value, and the average price per ton for the years 1913 to 1928, inclusive. Prior to 1913, the imports of lithopone were included in the figures for "zinc sulphide white."

With the entrance of the United States into the World War the imports of lithopone ceased entirely, the material having come principally from Germany. In 1919, when business relations were again restored, the United States imported only 739 tons, valued at $122,708, or the high price of $166.05 per ton; but in 1922 the imports had grown to 10,763 tons, valued at $885,671, or $82.29 per ton, representing less than half the price per ton of 1919. In 1923 the imports were 10,440 tons, valued, however, at only $776,383, or $74.37 per ton, and in 1924 they dropped to 6,830 tons, valued at $543,025, or $79.51 a ton. In 1928 they increased again to 9,885 tons, valued at $808,200, or $81.76 per ton.

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Table 7. - Lithopone imported for consumption into the United States, 1913-1928

Year	Quantity short tons	Value	Price per ton
1913	2,363	$146,474	$61.99
1914	3,990	271,310	68.00
1915	2,044	137,816	67.42
1916	2,341	405,730	173.31
1917	224	29,199	130.35
1918	-	-	-
1919	739	122,708	166.05
1920	1,714	263,240	153.58
1921	5,247	432,019	82.34
1922	10,763	885,671	82.29
1923	10,440	776,383	74.37
1924	6,830	543,025	79.51
1925	6,330	478,395	75.58
1926	8,686	661,700	76.18
1927	7,979	656,166	82.24
1928	9,885	808,200	81.76

Prior to 1922 the exports of lithopone from the United States were not separately recorded. Since that year, however, there has been a steady growth in our export trade in this commodity, as is shown in Table 8.

The declared export value per ton has been slightly above that of the domestic sales value and has followed closely the price trend of domestic sales.

Table 8. - Lithopone exported from the United States, 1922-1928.6/

Year	Short tons	Value	
		Total	Average
1922	1,616	$169,982	$105.19
1923	1,485	176,624	118.94
1924	923	104,783	113.52
1925	1,287	132,771	103.16
1926	1,941	200,412	103.25
1927	2,110	222,585	105.49
1928	3,326	337,523	101.48

6/ Not separately recorded prior to 1922.

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Correlation of Sales of Barium Pigments With Lead and Zinc Pigments

Lithopone, the principal barium pigment, has certain advantages over both white lead and zinc oxide. It is one of the whitest pigments known, and one of the finest in texture. Its opacity or hiding power is extremely high. It is easily mixed with other pigments, white or colored, and with various paint vehicles. It is entirely non-poisonous, and is not affected by sulphur fumes, either in the form of sulphur dioxide or hydrogen sulphide.

For exterior use, lithopone must be mixed with other white pigments, such as zinc oxide (lead-free or leaded) and some inert substances, such as magnesium silicate or silica, together with the proper oils and driers. A highly recommended composition consists of the following:- Lithopone, 45 per cent; zinc oxide, 40 per cent; and inerts, 15 per cent. These may vary, however, according to the formulas of the paint manufacturers, the lithopone and zinc oxide constituting from 80 to 85 per cent of the total pigment. A paint of this type ready to apply contains about 62 per cent of pigment and 38 per cent of vehicle (oil and thinner) and weighs approximately 15 pounds to the gallon.

Table 9 and figure 2 correlate the sales of barium pigments with the sales of lead and zinc pigments for the years 1910 to 1928.

Table 9. - Barium, lead, and zinc pigments sold by producers in the United States 1910-1928 (in short tons)

Year	Lithopone	Barium sulphate (blanc fixe)	Lead pigments 1/	Zinc pigments 2/
1910	3/ 12,655	(4)	143,810	5/ 50,592
1911	3/ 16,866	(4)	132,612	5/ 46,122
1912	3/ 24,220	(4)	146,833	5/ 64,032
1913	3/ 29,685	(4)	142,626	5/ 70,622
1914	3/ 32,819	(4)	159,474	5/ 70,619
1915	46,494	(4)	156,101	5/ 79,572
1916	51,291	1,229	128,979	5/ 90,276
1917	63,713	3,337	115,200	5/ 97,573
1918	62,403	9,522	102,888	5/ 102,778
1919	78,365	5,227	148,158	145,230
1920	89,373	8,046	158,107	129,904
1921	55,016	2,471	181,851	90,432
1922	83,360	7,349	208,756	148,078
1923	98,199	6,761	174,822	150,491
1924	109,469	7,796	202,066	158,199
1925	145,019	11,748	178,901	183,104
1926	159,931	(6)	162,084	170,782
1927	176,994	13,395	171,177	177,310
1928	200,468	19,081	169,947	185,129

1/ White lead (dry and in oil) and white lead sulphate.
2/ Zinc oxide and leaded zinc oxide.
3/ Marketed production.
4/ Not available.
5/ Zinc content of zinc pigment- domestic and imports.
6/ Bureau of Mines not at liberty ot publish figures.

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While the sales of lead pigments have been quite variable over this period, those of zinc and especially of lithopone have shown favorable increases.

The sales of lithopone during the pre-war period (1910 to 1913) averaged 20,856 short tons annually, while during the war period (1914 to 1918) they advanced to an average of 51,344 tons, an increase of 146 per cent. The post-war period sales averaged 119,619 tons annually, an increase of 133 per cent over the war period, and of 474 per cent over the pre-war period.

The sales of lead pigments, while larger, did not show such a tremendous growth. The average sale of lead pigments for the pre-war period (1910 to 1913) was 141,470 tons, or about 7 times that of lithopone for the same period. During the war, however, it decreased, the average being only 132,528 tons, or 6 per cent less than during the previous period. Since the war there has been only a relatively slight increase, the average sale for the years 1919 to 1928 being 175,587 tons, or about 24 per cent more than during the pre-war period.

The sales of zinc pigments, however, have been more favorable. During the pre-war period they averaged 57,842 tons, nearly three times that of lithopone and about one-third that of lead pigments. For the war period they increased to an average of 88,163 tons, or 34 per cent over the previous period, while from 1919 to 1928, inclusive, they averaged 153,866 tons, representing increases of 43 per cent over the war period and of 62 per cent over the pre-war period.

The tremendous growth in the lithopone industry, as compared with its two closest competitors, lead and zinc pigments, augurs well for the future of the industry.

BARIUM CHEMICALS

Preparation

Barium chemicals have important industrial uses in the United States. The most important of these chemicals are as follows: Blanc fixe, or precipitated barium sulphate (which, although practically identical with ground barite in chemical composition, has different physical properties), barium carbonate, chloride, nitrate, hydroxide, and dioxide.

Barium sulphide, which is prepared by heating a mixture of crude barite and some form of carbon (see p. 8), is used as the starting point for the preparation of barium chemicals.

Both barite and witherite are used in the United States as raw material for the manufacture of barium chemicals, but the quantity of the latter consumed for this purpose is relatively small and is largely imported from England. The manufacturers of barium chemicals prefer to use the washed, high-grade barite of the soft type, but they can and do use barite which could not be used in the preparation of the highest grades of ground barite.

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Barium carbonate is precipitated from a solution of barium sulphide by sodium carbonate (soda ash), and sodium sulphide is obtained as a by-product. Barium carbonate can also be prepared by passing a current of carbon dioxide gas through the solution of barium sulphide.

The method of producing blanc fixe or precipitated barium sulphate depends on the physical properties which are desired for the finished product. It was formerly made only by treating a solution of barium chloride with sodium sulphate, or sulphuric acid. It is now usually made by precipitation from a solution of barium sulphide by means of salt cake (sodium sulphate). This method produces a much denser product than that produced from barium chloride and in addition yields sodium sulphide as a valuable by-product. It is also made as a by-product of the manufacture of hydrogen peroxide when barium peroxide is treated with sulphuric acid. For certain color purposes blanc fixe is precipitated from hot, concentrated solutions, thus giving a crystalline product which is a valuable base for the manufacture of very brilliant colors.

Barium chloride may be produced by treating witherite (natural barium carbonate) with hydrochloric acid. It is usually produced in this country directly from crude barite by roasting with coal and calcium chloride. It may also be prepared by treating a solution of barium sulphide with calcium chloride.

Barium nitrate is produced by adding sodium nitrate (Chile saltpeter) either to a solution of barium chloride or to a solution of barium sulphide. It is also produced by dissolving witherite in a solution of nitric acid. The barium nitrate thus produced can be converted into barium oxide, dioxide, or hydroxide.

Barium hydroxide, or caustic barite, is prepared on a large scale by heating barium sulphide in earthenware retorts into which a current of moist carbonic acid is passed, after which superheated steam is passed over the resulting heated carbonate.

Barium peroxide, or dioxide, is prepared from either barium nitrate or barium carbonate. The barium nitrate, or carbonate, is first converted into barium oxide by heating in a closed apparatus, and the barium oxide is then converted into barium peroxide by heating at about 700° C. in a current of air free from carbon dioxide and moisture.

Whenever a sodium salt is added to a solution of barium sulphide in the preparation of barium salts, sodium sulphide is produced as a valuable by-product in addition to the desired barium product. This is an important product of the barium chemical industry, and has a large consumption by the American dye industry in the preparation of sulphur colors, especially sulphur black.

Figure 4 shows the steps, apparatus, and raw materials, used in the manufacture of barium chemicals.

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Uses

Blanc fixe, or permanent white, the precipitated barium sulphate, is the best grade of barium sulphate for pigment purposes, both as to whiteness and fineness of product. It is largely used where a pure white pigment or filler is desired, as in paints, rubber goods, linoleum, oilcloth, and glazed paper. It is also used in lithographic inks and as a base for lake colors. The battleship gray used extensively by the United States Navy contains about 45 per cent of blanc fixe. Under the name of chemically pure barium sulphate it is used as an indicator in X-ray photography.

Blanc fixe is placed on the market in pulp and as a dry powder. The pulp is a paste containing about 30 per cent of water, and is used chiefly by the paper and lithographic ink manufacturers. The dry powder is used for other pigment purposes.

Barium carbonate is a white insoluble salt which finds its largest use in the ceramics industry, where it is employed to prevent scumming on the surface of clay products and for the manufacture of optical glass, for which purpose a chemically pure product is required.

In the past various compounds of barium have been used to prevent the formation of scum, but at present they have practically all been replaced by barium carbonate. Nearly all of the soluble salts which cause this scum are sulphates, and calcium sulphate is by far the most troublesome in this respect. If a sufficient quantity of barium carbonate be added to a clay containing calcium sulphate, the calcium sulphate, which is a relatively soluble salt, will be broken up, but the products of the reaction, - barium sulphate and calcium carbonate, - being relatively insoluble, will not form a scum.

Barium carbonate is also used in growing quantities in the manufacture of flat wall paints. These paints, when containing about 45 per cent of precipitated barium carbonate, produce a velvety finish. Witherite (natural barium carbonate) can not be used for this purpose and should not be confused with precipitated barium carbonate. Barium carbonate is also used as a raw material for making barium peroxide and in the manufacture of certain kinds of enameled ironware.

Barium chloride is a white barium salt which is fairly soluble in water. It crystallizes with two molecules of water and is usually sold in the crystalline or powdered form. It is largely used in the manufacture of blanc fixe, lake colors, and as a mordant for fixing acid dyes on an inert base such as aluminum hydroxide or blanc fixe. Barium chloride is also used in the purification of salt, as a water softener, as a chemical reagent in sulphur determinations, to some extent in the ceramics industry, and in the manufacture of certain photographic chemicals. It has certain medicinal uses.

Barium nitrate is a soluble barium salt used principally for the manufacture of barium peroxide or dioxide. It is also used in pyrotechnics for making green fire and green signal lights and in the manufacture of certain explosives. It also has certain medicinal uses similar to those of barium chloride.

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Barium hydroxide, or caustic barite, has little commercial use in the United States. During periods of high prices for caustic potash, barium hydroxide is used to convert sulphate of potash into caustic potash. It has, until recently, been used in the refining of beet sugar, but as strontium or lime act in similar manner and are not poisonous, they have been substituted, especially the latter, for barium hydroxide. A small quantity, however, is still used in a western sugar refinery for this purpose.

Barium peroxide, or dioxide, finds its only use in this country in the manufacture of peroxide of hydrogen.

Barium monoxide is used for the preparation of barium peroxide, in the manufacture of certain varieties of optical glass, and in Europe in refining beet sugar.

Barium sulphide is the intermediate compound from which the majority of the other barium chemicals are made, and is one of the necessary materials in the manufacture of lithopone. It is also used with lime as a depilatory.

Barium chromate, lemon yellow, or yellow ultramarine, is used as a yellow pigment.

Barium chlorate is used in pyrotechnics and in dyeing.

Barium manganate has been used to some extent as a green pigment.

A mixture of barium sulphate, sulphide and carbonate has been patented by E. E. Fisher (United States Patents 1,665,693 and 1,665,694) for use in mixes for the manufacture of pressed or blown glass ware. This mixture is claimed to be particularly beneficial where sharp corners and intricate patterns have to be completely filled. The barium chemicals used in glass making must be virtually free from iron, silica and dolomite.

Production and Sales

Prior to the World War the United States was almost wholly dependent on imports for its supply of barium chemicals. There was practically no domestic production of the barium salts such as barium dioxide, chloride, nitrate, and blanc fixe. At that time the only chemical product manufactured in this country on a large scale which utilized barite as a raw material was lithopone. The shutting off of imports with the outbreak of the war gave a great stimulus to the establishment of a barium chemical industry in the United States. In addition there were large war demands for certain barium salts (barium peroxide, blanc fixe, and barium nitrate), which greatly increased the domestic production and tended to develop an industry in the United States.

According to Table 10 and figure 1 the use of crude barite for the manufacture of barium chemicals has not shared the increases exhibited in the ground barite or lithopone industries. At no time has the percentage of crude barite used in the chemical industry exceeded 25 per cent of the total used in all industries, and generally it has been much less.

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During the period from 1915 to 1920, inclusive, the barium chemical industry consumed on an average of 24,442 short tons annually of both domestic and imported barite, 18 per cent of that used in all industries.

The average annual consumption of crude barite, both domestic and imported, in the chemical industry during the period from 1921 to 1928, inclusive, was 31,074 tons, an increase of 27 per cent over the preceding period (1915-1920), but only 13 per cent of the total used in all industries.

Table 10. - Crude barite, both domestic and imported, used in the manufacture of barium products, 1915-1928 (in short tons)

Year	Used in barium chemicals	Total used	Per cent of total
1915	10,216	108,622	9
1916	38,283	185,688	20
1917	49,842	196,039	25
1918	38,041	185,763	20
1919	32,976	201,586	16
1920	37,210	229,443	16
1921	10,952	100,607	11
1922	25,303	167,842	15
1923	34,327	210,587	16
1924	33,181	213,163	16
1925	29,141	232,685	13
1926	33,119	281,056	12
1927	34,280	330,190	10
1928	48,289	334,695	14

Tables 11 and 12 show the marketed production of the principal barium chemicals in the United States over a period of years. The total marketed production has registered a steady growth since the world-wide depression year of 1921 and during 1927 and 1928, has exceeded the sales of barium chemicals of any year prior to 1921. The total value has shown an upward trend, although the price per ton has decreased far below that obtaining during and preceding the war.

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Table 11. - Marketed production of barium chemicals[1] in the United States, 1915-1928, in short tons

Year	Quantity	Value	Price per ton
1915	8,823	(2)	(2)
1916	16,792	$1,962,520	$116.87
1917	22,503	(2)	(2)
1918	23,186	(2)	(2)
1919	20,013	1,519,788	75.94
1920	20,760	1,743,634	83.99
1921	5,487	412,275	75.14
1922	13,901	1,562,216	112.38
1923	16,803	1,231,646	73.30
1924	18,154	1,213,900	66.87
1925	18,654	1,207,770	64.75
1926	21,911	1,325,262	60.48
1927	23,943	1,517,994	63.40
1928	33,969	2,045,156	60.21

1/ Barium chemicals include dioxide, carbonate, chloride, hydroxide, nitrate, sulphate (blanc fixe), and sulphide.
2/ Not available.

Of the barium chemicals sold in the United States, blanc fixe, or precipitated barium sulphate, is by far the most important. During recent years this commodity has accounted for about 33 per cent of the total quantity of the barium chemicals sold. Barium carbonate is the next important of the chemicals and accounts for about 25 per cent of the total.

Table 12. - Barium chemicals sold by producers in the United States, 1918-1928, in short tons

Year	Barium carbonate	Barium chloride	Barium sulphate (blanc fixe)	Other barium chemicals 1/	Total
1918	7,661	4,530	9,522	1,473	23,186
1919	2/ 7,135	4,509	5,227	3,142	20,013
1920	7,484	3,084	8,046	2,146	20,760
1921	1,956	(3)	2,471	1,060	5,487
1922	2,281	2,022	7,349	2,249	13,901
1923	6,362	3,301	6,761	379	16,803
1924	6,058	3,859	7,796	441	18,154
1925	4,962	(3)	11,748	1,944	18,654
1926	5,394	4,592	(3)	11,925	21,911
1927	5,969	3,708	13,395	871	23,943
1928	7,626	5,224	19,081	2,038	33,969

1/ Figures for "other barium chemicals" cover different chemicals for each year.
2/ Figures for 1919 cover production, not sales.
3/ Included under "other barium chemicals."

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Markets and Prices

The barium chemical industry in the United States is well situated as regards markets. The demand for barium chemicals is more limited than that for lithopone or other barium products, and the plants are generally located near their market instead of at the source of raw material, though several are in fairly close promimity to domestic deposits.

The chief markets for barium chemicals are in the East, and the industry comes into direct competition with foreign products, which prior to the war satisfied fully two-thirds of the domestic requirements. The eastern plants are so situated that they are able to use either domestic or imported barite for their needs, and are thus able to furnish their market at the lowest possible price.

The barium chemical industry in the Mid-Western States use the locally produced barite and distribute the finished products to the market areas to the north and west of them.

The western producer of barium chemicals finds his market in the immediate vicinity, and has no competition from either Mid-Western or imported barium chemicals.

The prices of certain barium chemicals are shown in Table 14, for the years 1922 to 1928, inclusive.

Imports and Exports

Table 13 shows the imports for consumption of certain barium chemicals for the years 1902 to 1928, inclusive. There has been a general increase in practically all items, with witherite, blanc fixe, and barium nitrate showing the larger gains. The war curtailed our imports to a great extent, and it was not until 1920 that they returned to anything like the pre-war levels.

Prior to the war practically 90 per cent of the imports of barium chemicals into the United States were represented by three barium salts--namely, precipitated barium carbonate, barium chloride and barium dioxide. Within recent years, however, there has been a considerable growth in the imports of natural barium carbonate, blanc fixe, and barium hydroxide, until they represent nearly one-half of the total imports of barium chemicals.

Previously, these chemicals were generally imported from Germany, but now England, Belgium, and Italy furnish nearly one-half of our import trade in them. Our requirements of witherite, however, are furnished almost solely by England.

It is a question whether the near future will see the same steady growth in the importation of barium chemicals (excepting witherite) as has taken place during recent years. The industry in this country seems now to be on a firm economic and financial basis and able to take care of domestic

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requirements, furnishing the consuming markets with products equally as good and at prices comparable with the imported products. Figure 5 shows the location of barite deposits and barium products plants in the United States.

Table 13. - Value of barium compounds imported into the United States, 1902-1928.

Year	Witherite, barium carbonate		Barium binoxide	Barium chloride	Blanc fixe	Barium nitrate	Barium hydroxide
1902	$12,777		$66,746	$46,905	$25,933	-	-
1903	25,762		84,549	68,762	35,466	-	-
1904	46,133		102,076	43,694	50,901	-	-
1905	45,073		111,856	47,386	53,112	-	-
1906	55,405		152,403	65,242	61,961	-	-
1907	24,552		167,519	79,333	85,713	-	-
1908	22,159		181,533	42,291	73,131	-	-
1909	31,584		255,013	47,352	65,427	-	-
1910	25,229		341,631	35,614	67,975	-	-
1911	27,351		270,917	28,896	71,049	-	-
(1)	Natural	"Precipitated barium carbonate"					
1912	$15,777	$ 9,938	252,320	27,655	70,327	-	-
1913	13,116	38,949	239,000	37,620	62,785	-	-
1914	8,084	28,221	332,709	68,866	32,619	-	-
1915	12,165	2,786	218,776	31,295	18,501	-	-
1916	18,169	-	6,590	608	17,810	-	-
1917	17,321	1,554	-	-	3,333	-	-
1918	14,134	-	-	-	-	-	-
1919	4,739	2,666	-	19,846	90	-	-
1920	61,284	37,462	64,447	151,778	8,485	-	-
1921	25,188	80,603	127,631	72,621	22,470	-	-
1922	39,114	210,250	189,334	112,785	76,445	$16,795 2/	$6,573 2/
1923	41,823	79,482	152,270	75,014	32,063	59,766	16,872
1924	56,415	128,217	120,374	100,810	50,465	54,638	8,241
1925	63,634	160,164	70,553	67,306	81,439	58,192	5,605
1926	80,679	189,167	8,157	49,426	136,697	49,494	9,789
1927	65,821	119,014	1,264	45,285	107,179	65,284	12,439
1928	82,434	116,241	1,310	25,253	168,923	69,010	10,031

1/ Figures prior to 1912 included both "natural" and "precipitated barium carbonate."

2/ Not separately recorded prior to the tariff of Sept. 22, 1922.

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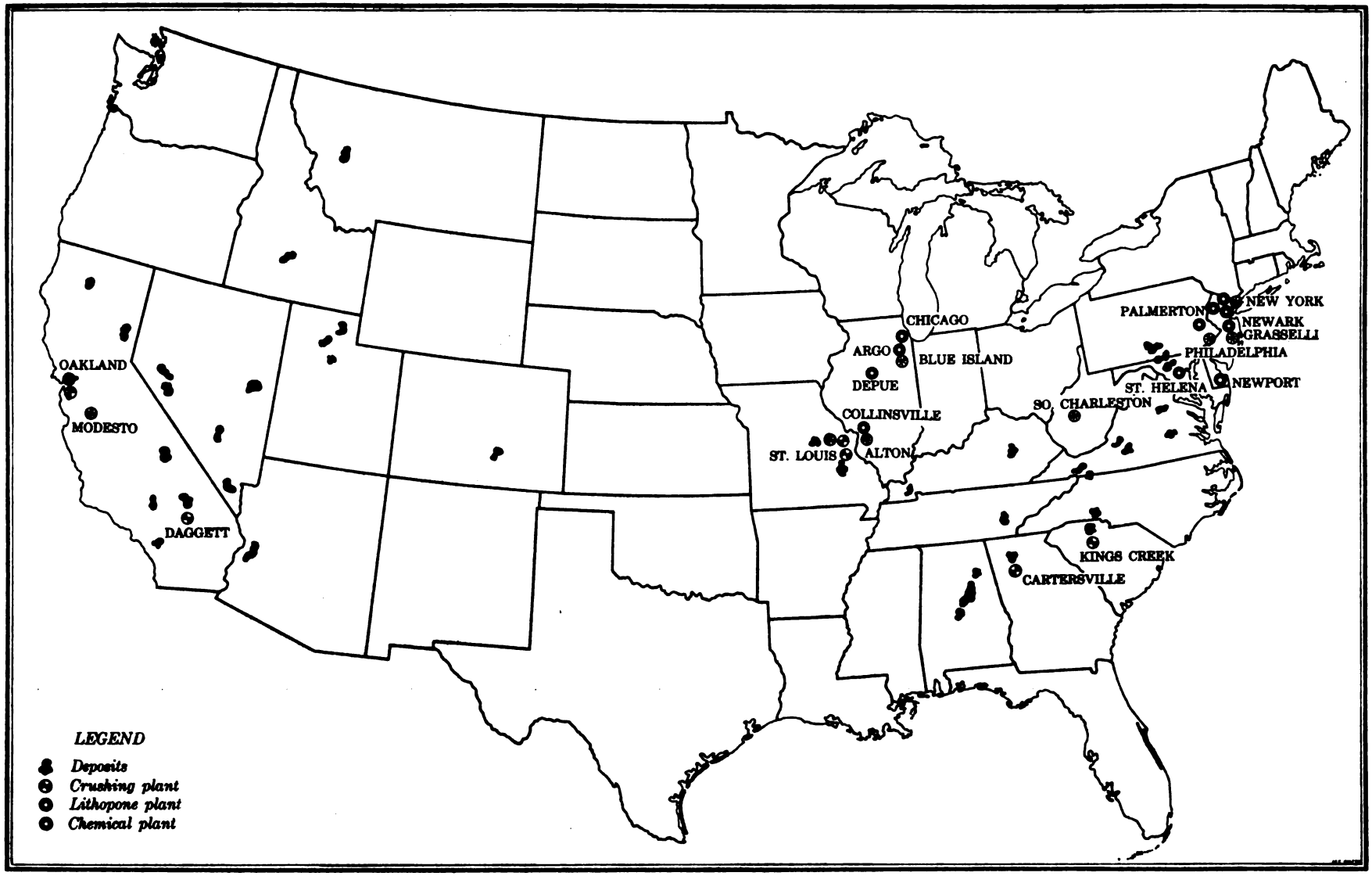

Figure 5. – Location of barite deposits and barium products plants

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Table 14. - Prices of barite and barium products 1/

		1922	1923	1924	1925	1926	1927	1928
Barite, crude (short ton)	High	$ 7.25	$ 7.77	$ 9.00	$8.50	$8.50	$8.00	$7.50
	Low			8.00		8.00		6.50
Barite, ground (short ton)	High	26.00	28.00	26.00	23.00	23.00	23.00	23.00
	Low	23.00	25.00	22.00	22.000			
Blanc fixe (dry) (pound)	High	.04¼	.04¼	.05	.05	.04½	.04 3/8	.04½
	Low			.04	.04	.04	.04¼	.03 5/8
Blanc fixe(pulp) (short ton)	High	50.00	60.00	70.00	70.00	65.00	65.00	$60.00
	Low	40.00	40.00	50.00	55.00	53.00	60.00	40.00
Barium carbonate (short ton)	High	85.00	90.00	90.00	65.00	55.00	54.00	60.00
	Low	48.00	66.00	63.00	54.00	50.00	48.00	47.50
Barium chlorate (pound)	High	.45	.15	.15	.15	.15	.15	.15
	Low	.14	.14	.14	.14	.14	.14	.14
Barium chloride (short ton)	High	115.00	100.00	95.00	72.50	66.00	65.00	$70.00
	Low	50.00	80.00	70.00	60.00	60.00	52.00	54.00
Barium nitrate (pound)	High	.10¼	.10¼	.10	.09	.09	.10	.08½
	Low	.06	.07½	.08	.08	.07½	.07½	.08¼
Lithopone (pound)	High	.06¼	.07¼	.08 5/8	.06 5/8	.06 5/8	.05 7/8	.05 7/8
	Low	.06	.06	.06 3/8	.06 1/3	.05 7/8		.05¾

1/ Quotations on crude and ground barite are taken from Engineering and Mining Journal Press. Other quotations from Oil, Paint and Drug Reporter. The following are the designations, on which quotations in the preceding table are based:-

Crude barite, "f.o.b. mines."
Ground barite, "domestic, including barrels, f.o.b., St. Louis."
Lithopone, "in barrels, l.c.l."
Barium carbonate, "bags, works."
Barium chlorate, "kegs."
Barium chloride, "crystals, bags."
Barium nitrate, "casks."
Barium sulphate (blanc fixe), "dry, in barrels, l.c.l."
Barium sulphate (blanc fixe), "pulp works."

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The following is a list of producers of ground barite and barium products:

GROUND BARITE

Name and Address of Company	Location of Plant
Chemical & Pigment Co. (Inc.), Oakland, Calif.	Oakland, Calif.
Clinchfield Sand & Feldspar Co., Baltimore, Md.	Kings Creek, S. C.
C. P. DeLore Co., St. Louis, Mo.	Miss. River & River Des Peres, St. Louis, Mo.
Flynt Silica & Spar Co., Los Angeles, Calif.	Daggett, Calif.
National Pigments & Chemical Co., St. Louis, Mo.	St. Louis, Mo.
Thompson, Weinman & Co., New York, N. Y.	Cartersville, Ga.

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LITHOPONE

Name and Address of Company	Location of Plant
Chemical & Pigment Co. (Inc.), Oakland, Calif.	Oakland, Calif.
Chemical & Pigment Co. (Inc.), Oakland, Calif.	Collinsville, Ill.
Chemical & Pigment Co. (Inc.), Oakland, Calif.	St. Helena, Md.
E. I. du Pont de Nemours & Co., Wilmington, Del.	Newark, N. J.
E. I. du Pont de Nemours & Co., Wilmington, Del.	Philadelphia, Pa.
Eagle-Picher Lead Co., Chicago, Ill.	Argo, Ill.
Grasselli Chemical Co., Cleveland, Ohio.	Grasselli, N. J.
Krebs Pigment & Chemical Co., Newport, Del.	Newport, Del.
Mineral Paint Zinc Co., New York, N. Y.	Depue, Ill.
New Jersey Zinc Co. (of Pennsylvania), New York, N. Y.	Palmerton, Pa. (2 plants)
Sherwin-Williams, Cleveland, Ohio.	Chicago, Ill.
United Color & Pigment Co., Newark, N. J.	Newark, N. J.

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BARIUM CHEMICALS[5/]

Name and Address of Company	Location of Plant
Alton Barium Products Co., Alton, Ill.	Alton, Ill.
Barium Products (Inc.), Modesto, Calif.	Modesto, Calif.
Barium Reduction Corporation, Charleston, W. Va.	So. Charleston, W. Va.
Chicago Copper & Chemical Co., Chicago, Ill.	Blue Island, Ill.
E. I. du Pont de Nemours & Co., Wilmington, Del.	Philadelphia, Pa.
Grasselli Chemical Co., Cleveland, Ohio.	Grasselli, N. J.
Oakland Chemical Co., New York, N. Y.	New York, N. Y.
Titanium Pigment Co. (Inc.), New York, N. Y.	Carondelet Station, St. Louis, Mo.

5/ Includes only those using barite.

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